

IEA Agreement on the Production and Utilization of Hydrogen



2001 Annual Report

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Overview: International Energy Agency Hydrogen Implementing Agreement

The International Energy Agency

The International Energy Agency (IEA) was established in 1974, following the first oil crisis and is managed within the framework of the Organization for Economic Cooperation and Development (OECD). The mission of the IEA is to facilitate collaborations for the economic development, energy security, environmental protection and well-being of its members and of the world as a whole. The IEA is currently comprised of twenty-five member countries, ten of which are participants in the program focused on the Utilization and Production of Hydrogen.

The Hydrogen Program, or Implementing Agreement, has been in existence for more than twenty years for the purpose of advancing hydrogen technologies and accelerating hydrogen's acceptance and widespread utilization. Past collaborations have been in the areas of Thermochemical Production, High Temperature Reactors, Electrolysis, Storage, Safety, and Markets.

The following countries/organizations participate in the Hydrogen Implementing Agreement: Canada, European Commission, Japan, Lithuania, the Netherlands, Norway, Spain, Sweden, Switzerland and the United States.

GUIDING PRINCIPLES OF THE HYDROGEN AGREEMENT

Today, hydrogen is primarily used as a chemical feedstock in the petrochemical, food, electronics, and metallurgical processing industries, but is rapidly emerging as a major component of clean sustainable energy systems. It is relevant to all of the energy sectors - transportation, buildings, utilities, and industry. Hydrogen can provide storage options for intermittent renewable technologies such as solar and wind, and, when combined with emerging decarbonization technologies, can reduce the climate impacts of continued fossil fuel utilization. The members of the IEA Hydrogen Program agree that energy related hydrogen technologies, thus, merit serious attention. The following are the guiding principles on which the scope of the Agreement is based:

- Hydrogen--now mainly used as a chemical for up-grading fossil-based energy carriers--will in the future increasingly become an energy carrier itself. It is necessary to carry out the analysis, studies, research, development and dissemination that will facilitate a significant role for hydrogen in the future.
- Significant use of hydrogen will contribute to the reduction of energy-linked environmental impacts, including global warming due to anthropogenic carbon emissions, mobile source emissions such as CO, NO_x, SO_x, and NMHC (non-methane hydrocarbons), and particulates.
- Hydrogen can be used as a fuel for a wide variety of end-use applications including important uses in the transportation and utility sectors.

- Hydrogen is currently used to up-grade lower quality, solid and liquid fossil fuels, such as coal and heavy oils. The use of hydrogen in such applications reduces harmful emissions through more efficient end-use conversion processes and extends the range of applicability. Ultimately, with the addition of hydrogen, carbon dioxide emissions can be used to produce useful chemicals and fuels.
- Hydrogen has the potential for short, medium and long-term applications and the steps to realize the potential for applications in appropriate time frames must be understood and implemented.
- All sustainable energy sources require conversion from their original form. Conversion to electricity and/or hydrogen will constitute two prominent, complimentary options in the future.
- Hydrogen can assist in the development of renewable and sustainable energy sources by providing an effective means of storage, distribution and conversion; moreover, hydrogen can broaden the role of renewables in the supply of clean fuels for transportation and heating.
- Hydrogen can be produced as a storable, clean fuel from the world's sustainable non-fossil primary energy sources - solar, wind, hydro, biomass, geothermal, nuclear, or tidal. Hydrogen also has the unique feature that it can upgrade biomass to common liquid and gaseous hydrocarbons, thus providing a flexible, sustainable fuel.
- All countries possess some form of sustainable primary energy sources; hence, hydrogen energy technologies offer an important potential alternative to fossil fuel energy supply (in many instances to imported fuels). Utilization of hydrogen technologies can contribute to energy security, diversity and flexibility.
- Barriers, both technical and non-technical, to the introduction of hydrogen are being reduced through advances in renewable energy technologies and hydrogen systems including progress in addressing hydrogen storage and safety concerns.
- Hydrogen energy systems have potential value for locations where a conventional energy supply infrastructure does not exist. The development of hydrogen technologies in niche applications will result in improvements and cost reductions that will lead to broader application in the future.

The members of the IEA Hydrogen Agreement recognize that a long-term research and development effort is required to realize the significant technological potential of hydrogen energy. This effort can help create competitive hydrogen energy production and end-use technologies, and supports development of the infrastructure required for its use. Attention is to be given to the entire system, in particular all of the key elements should be covered either with new research or based on common knowledge.

If the technological potential of hydrogen is realized, it will contribute to the sustainable growth of the world economy by facilitating a stable supply of energy and by helping to reduce future emissions of carbon dioxide. Cooperative efforts among nations can help speed effective progress towards these goals. Inasmuch as hydrogen is in a pre-commercial phase, it is

particularly suited to collaboration as there are fewer proprietary issues than in many energy technologies.

IEA Hydrogen Vision: Our vision for a hydrogen future is one based on clean sustainable energy supply of global proportions that plays a key role in all sectors of the economy.

IEA Hydrogen Mission: The mission of the IEA Hydrogen Program is to accelerate hydrogen implementation and widespread utilization.

IEA Hydrogen Strategy: Our strategy is to facilitate, coordinate and maintain innovative research, development and demonstration activities, through international cooperation and information exchange.

We will achieve this strategy by meeting the below listed objectives:

Technology Objective:

Promote acceptance of hydrogen as an energy carrier.

Actions:

- Conduct research and development activities to address important barriers to hydrogen's acceptance.
- Foster and maintain a balanced portfolio of hydrogen technologies.
- Develop safe, efficient, and cost-effective hydrogen storage systems.
- Demonstrate integrated hydrogen systems.
- Collect, disseminate, and analyze information on hydrogen technologies.
- Develop direct hydrogen production technologies.

Energy Security Objective:

Contribute to global energy security.

Actions:

- Facilitate the transition from fossil fuel energy systems to sustainable hydrogen-based energy systems.
- Provide resources for the conversion of intermittent and seasonal renewables to base-load, load-following or peak-load power supplies, and to transportation fuels.
- Assist developing countries in evaluating sustainable, indigenous resources for hydrogen production.

Deployment Objective:

Promote deployment of hydrogen technologies with important local and global energy benefits.

Actions:

- Provide design support for hydrogen demonstrations.
- Conduct cost-shared and task-shared deployment activities for hydrogen energy systems.
- Act as an information resource for on-going and proposed hydrogen demonstration activities, including performance analyses.
- Conduct case studies for hydrogen systems in developing countries.

Environmental Objective:

Exploit the environmental benefits of hydrogen.

Actions:

- Carry out research and development on renewable hydrogen production techniques.
- Promote hydrogen as a "clean" fuel.
- Perform life cycle assessments of hydrogen technologies and energy systems.
- Conduct research and development on technologies that lead to the decarbonization of fossil fuels.

Economic Objective:

Develop cost-effective hydrogen energy systems that can compete in global markets.

Actions:

- Encourage industry participation to obtain market-oriented input for the prioritization of research, development and demonstration activities.
- Develop and utilize analysis tools to evaluate and optimize hydrogen systems.
- Increase involvement of industry in the Agreement's activities.
- Foster clean system incentive policies.
- Identify secondary benefits of hydrogen energy systems, such as demilitarization.

Market Objective:

Identify and overcome barriers for hydrogen's penetration into the energy and fuel markets.

Actions:

- Contribute to the scientific and technical basis for approved codes and standards.
- Promote hydrogen infrastructure for supply, maintenance and operation.
- Pursue technologies that will lead to Increased market penetration for hydrogen.
- Initiate safety-related educational and technology assessment activities.

Outreach Objective:

Advertise the benefits of hydrogen.

Actions:

- Increase involvement of private and public organizations in the Hydrogen Program.
- Utilize media tools to promote hydrogen education.
- Establish collaborative research and development projects that promote international networks.
- Collaborate with other IEA Agreements to increase the effectiveness of crosscutting research and development activities.
- Increase cooperation to reach "critical mass" in research and development activities.

Summary

As we enter the new millennium, concerns about global climate change and energy security create the forum for mainstream market penetration of hydrogen. Ultimately, hydrogen and electricity, our two major energy carriers, will come from sustainable energy sources, although, fossil fuel will likely remain a significant and transitional resource for many decades. Our vision for a hydrogen future is one of clean sustainable energy supply of global proportions that plays a key role in all sectors of the economy. We will implement our vision with advanced technologies including direct solar production systems and low-temperature metal hydrides and room-temperature carbon nanostructures for storage.

Current and Completed Annexes of the IEA Hydrogen Implementing Agreement

| | | |
|----------|---|-----------|
| Annex 1 | Thermochemical Production | 1977-1988 |
| Annex 2 | High Temperature Reactors | 1977-1979 |
| Annex 3 | Assessment of Potential Future Markets | 1977-1980 |
| Annex 4 | Electrolytic Production | 1979-1988 |
| Annex 5 | Solid Oxide Water Electrolysis | 1979-1983 |
| Annex 6 | Photocatalytic Water Electrolysis | 1979-1988 |
| Annex 7 | Storage, Conversion and Safety | 1983-1992 |
| Annex 8 | Technical and Economic Assessment of Hydrogen | 1986-1990 |
| Annex 9 | Hydrogen Production | 1988-1993 |
| Annex 10 | Photoproduction of Hydrogen | 1995-1998 |
| Annex 11 | Integrated Systems | 1995-1998 |
| Annex 12 | Metal Hydrides for Hydrogen Storage | 1995-2000 |
| Annex 13 | Design and Optimization of Integrated Systems | 1999-2001 |
| Annex 14 | Photoelectrolytic Production of Hydrogen | 1999-2001 |
| Annex 15 | Photobiological Production of Hydrogen | 1999-2001 |
| Annex 16 | Hydrogen from Carbon-Containing Materials | 2002-2004 |
| Annex 17 | Solid and Liquid State Hydrogen Storage Materials | 2001-2003 |

REPORT OF THE CHAIRMAN

Mr. Neil P. Rossmeissl
U.S. Department of Energy

[Note – The IEA Hydrogen Agreement Fall Executive Committee meeting had to be cancelled due to travel restrictions following the events of September 11, 2001. As a result, Mr. Rossmeissl's term as Chairman was extended until the formal election could be held. That election was held on March 18, 2002 at which time Mr. Trygve Riis of the Research Council of Norway was unanimously elected to serve a three-year term as Chairman of the Executive Committee. Two Vice Chairmen, Mr. Nick Beck of Natural Resources Canada and a second to be confirmed at the Fall 2002 Executive Committee Meeting, will support Mr. Riis. The Executive Committee extends its gratitude to Mr. Rossmeissl for his years of leadership and for his graciousness in continuing his duties during the election delays of the past year.]

INTRODUCTION

Interest in hydrogen technologies has never been stronger. As discussions continue about global climate change, there is, at least, agreement that carbon emissions must be reduced. How this can, or should be accomplished is still under discussion; however, most agree that something must be done. More and more, we are recognizing the consequences of our continued dependency on oil, particularly to our environment. Hydrogen is no longer just a good idea, but a necessity for our future.

Every nation possesses domestic resources that can be used to produce hydrogen in an environmentally responsible manner. Infrastructure exists that can be used and expanded to begin using hydrogen in our energy sectors. Fuel cell technologies continue to mature. In the interim, internal combustion engines can be used in both the stationary and mobile markets to begin realizing the benefits of hydrogen fuel and to help build hydrogen's market share in the energy markets. As demand and production increase, we will see the cost of hydrogen technologies come down to the point where hydrogen is not only the environmental choice, but also the economical one.

Much has been learned about the design, construction, operation and maintenance of integrated hydrogen energy systems through successful demonstrations worldwide. These demonstrations help build public confidence in hydrogen technologies and show policy makers that hydrogen systems can be operated efficiently and safely. The SunLine Transit Agency in California, for the last several years, has hosted one of the world's most complex integrated hydrogen systems. Hydrogen is produced from both fossil and renewable resources, stored, dispensed at a public access fueling island and used for public and private transit. Public outreach, education and training are high priorities, including establishment of a hydrogen system-specific curriculum at the local community college. BMW has taken their Clean Energy World Tour around the globe, developing a following for hydrogen technologies in their wake and showing us all how the benefits of hydrogen need not wait for the fuel cell. The Clean Urban Transportation in Europe (CUTE) project will provide one of the most comprehensive bases of information for hydrogen fuel cell public transit vehicles. No other project encompasses the level of diversity of this monumental undertaking. The buses will be exposed

to different climates and driving conditions, as well as different production and delivery methods for the hydrogen. The project will clearly show how existing infrastructure can be used to provide the hydrogen fuel and will expose a great number of people to the benefits of hydrogen systems. All of us in the hydrogen community commend the European Commission and host nations for launching this project. We will follow the project closely and look forward to the coming successes. Those that are mentioned here, as well as the many other projects around the world, are important steps for realizing a future where hydrogen plays an important and vital role in the energy sector. Our members and experts will continue to provide whatever support they can to these efforts and our Agreement will continue to capture and disseminate the findings from these important demonstration projects.

MEMBERSHIP

We continue to focus on increasing the impact of our Agreement's activities through expanding our membership. At our Spring Executive Committee meeting, we were pleased to again have Dr. Kornel Kovacs from the A. Jozsef University of Szeged, Hungary, participate as an observer. Dr. Kovacs also continued his valuable contributions to our Task 15, Photobiological Hydrogen Production. Dr. Kovacs graciously planned to host our Fall meeting, where we had hoped to lay the final groundwork for making Hungary an official Participation in the Hydrogen Agreement. I would like to express our sincere appreciation to Dr. Kovacs for his flexibility and understanding as we tried to reschedule and, ultimately, cancel the Fall meeting. Hopefully, we can make up for this during 2002 and see Hungary become an official member of our Agreement by 2003.

The United Kingdom was also represented at our Spring Executive Committee meeting. Dr. Barry Lakeman (Defence Science and Technology Laboratory, UK) participated on behalf of the UK Department of Trade and Industry. The UK has a number of carbon and metal hydride projects that will compliment our Task 17, Solid and Liquid State Hydrogen Storage Materials, as well as expertise in a number of hydrogen production areas. We are hopeful that the UK will officially rejoin the Hydrogen Agreement in Spring 2002.

We continue to work with representatives from several other countries to further increase our Membership.

STATUS OF TASKS

Task 13 - Design and Optimization of Integrated Systems

Task 13 concluded its activities in December 2001. Our Operating Agent and experts are now hard at work completing the final report. This was an extremely productive activity. The results of the three case studies have been presented at several international meetings. I would like to commend our experts for another exceptional integrated systems Task. The tools and guidelines that have been developed will be very useful for planning, designing and optimizing hydrogen demonstrations. Special thanks go to our Operating Agent, Mrs. Catherine Gregoire Padró of the National Renewable Energy Laboratory, USA, and to her experts for another outstanding activity.

Task 14 - Photoelectrolytic Production of Hydrogen

We have nearly completed this three-year effort. Conversion efficiencies have now topped 16% with the gallium-based system and 8% with the lower-cost silicon-based systems. We are learning a great deal about system configurations and materials and have demonstrated that novel design improvements can significantly lower efficiency losses and, ultimately, cost. Although much work must still be done, we are nearing the point where a system can be selected for larger-scale engineering testing. This activity will be extended for an additional two years in order to further advance the work and to begin an engineering scale-up.

Task 15 - Photobiological Production of Hydrogen

This three-year effort is also nearing its completion. Some very significant progress has been made. Our experts have demonstrated sustainable photobiological production of molecular hydrogen using the green alga *Chlamydomonas reinhardtii*. Genetic modifications to various microalgae strains have progressed, resulting in improved oxygen tolerance and conversion efficiencies. This work is still in the very early development stage. However, our experts have already seen efficiencies around our 3% target. Our fermentation efforts are also progressing, with some very high carbohydrate conversion efficiencies being reported. The Netherlands has now formally joined Task 15 and is contributing in a number of areas including fermentation and bioreactor development. The experts continue to work very closely with the European COST 8.41 Network. A joint meeting was held in Budapest in September. The results from this three-year effort will be highlighted at next year's BioHydrogen 2002. Based on the good progress that has been made and the added Participants (the UK is also expected to join), this Task will also be extended for another two years.

Task 16 - Hydrogen from Carbon Containing Materials

The Task Development efforts are now complete for this new activity. Three subtasks have been defined: A) Large-Scale Hydrogen Production, B) Biomass to Hydrogen and C) Small Stationary Reformers. The Greenhouse Gases Agreement (GHG) will lead Subtask A. Subtask B will collaborate very closely with the Gasification and Pyrolysis activities of the Bioenergy Agreement. This will be the first Task that is led by Industry. A number of industry participants have also been confirmed for each of the three subtasks. Formal Task approval is expected at our next Executive Committee meeting. I would like to thank Mr. Bjorn Gaudernack and Mrs. Elisabet Fjermestad Hagen for their hard work in bringing this effort together and for developing the collaboration with the GHG.

Task 17 - Hydrogen Storage in Metal Hydrides and Carbon

We have completed the first year of this follow-on to our extremely successful Task 12. The Task consists of twenty-seven collaborative projects to develop carbon and metal hydride materials for hydrogen storage. Currently, there are no chemical hydride projects included, although some may be added at a later date. Our experts are already making a great deal of progress, particularly in the further advancement of the alanates that were responsible for achieving the targets laid out in Task 12. We also have several projects targeted at validating some of the results reported for the carbon materials and understanding the fundamental science that can lead to these high storage capacities.

HIGHLIGHTS FROM THE 2001 EXECUTIVE COMMITTEE MEETINGS

45th Meeting, The Hague, Netherlands, 8-11 May 2001

- In conjunction with the meeting, the Committee visited the Sustain 2001 Exposition in Amsterdam. In addition to visiting with exhibitors at Sustain, the group was given an overview on plans for renewable energy systems by a representative from Nuon, the Netherlands' largest energy service provider.
- The ExCo discussed possible activities that could accelerate the introduction of hydrogen technologies into the market. It was agreed that the industry-led hydrogen associations would be the ideal resource for developing market acceleration strategies. A subcommittee was formed to develop an outline for holding a joint hydrogen association workshop.
- Dr. Barry Lakeman from the United Kingdom Defence Science and Technology Laboratory presented a very informative overview of the hydrogen-related activities in the United Kingdom.
- Mr. Toshiaki Abe and Dr. Katsuhide Ōhira of NEDO were welcomed as the new Executive Committee Member and Alternate, respectively, for Japan.
- Dr. Henk Barten of NOVEM was welcomed as the new Alternate for the Netherlands.

OTHER ACTIVITIES

As mentioned earlier, a number of hydrogen demonstration projects have taken place or are underway worldwide. Several more are planned for the coming years. Our Annex 11 Final Subtask Report, Case Studies of Integrated Hydrogen Energy Systems, serves as the only collection of comprehensive reports available and the experience gained from these demonstration projects has proven invaluable. Last year our Executive Committee commissioned Dr. Thomas Schucan, the author of the Annex 11 Report, to prepare an additional set of case study reports. Working closely with the demonstration project leaders, Dr. Schucan has made good progress in preparing draft reports that are now being reviewed and discussed by our Annex 13 experts. Emphasis was again placed on safety, permitting and lessons learned, as well as technical challenges. The final reports will be published on our IEA Web site (www.eren.doe.gov/hydrogen/iea) during this coming year. We expect to continue this effort to capture the lessons learned from these important international demonstrations and to make this resource available to the hydrogen community.

The International Conference on the Hydrogen Age of Asia took place 27-28 November 2001 in Tokyo, Japan. What started as a modest effort to understand the feasibility and technical challenges of large-scale, long-distance hydrogen pipelines grew into this important and well-attended (over 500 participants) meeting. Dr. Hirata and his colleagues have worked very hard to raise awareness of the opportunities for hydrogen pipeline and to grow the number of stakeholders for hydrogen technologies in Asia. We were pleased to be able to support this meeting by sending our Executive Committee Member from Norway, Mr. Trygve Riis, to present an overview of the IEA Hydrogen Agreement and to discuss future opportunities for collaboration.

Our integrated systems experts have begun development efforts for a new Task to follow-on the progress made during our Tasks 11 and 13. Task Development Workshops will be held during 2002 to solicit input from a larger audience of technical experts and stakeholders and to begin outlining what we expect to become the new Task 18. We hope to have the Programme of

Work ready for approval at our Fall 2002 Executive Committee Meeting and to begin work in early 2003.

WORLD HYDROGEN ENERGY CONFERENCE

The World Hydrogen Energy Conference (WHEC) will be held 9-13 June 2002 in Montreal, Quebec, Canada. This biannual meeting is an important technical forum for hydrogen. This year's meeting is expected to be one of the largest as both the Canadian and the National (U.S.) Hydrogen Associations are forgoing their respective annual meetings in order to focus their support for and participation in the 2002 WHEC. Many of our experts will be presenting and/or chairing sessions at the meeting. Our Executive Secretary, Ms. Carolyn Elam, will be presenting an overview of our Agreement's activities and Dr. Thomas Schucan will present some of the results from our Case Studies effort.

SUMMARY

Special recognition goes to Dr. Antoon Kipperman of the Netherlands for his many years of service to the Executive Committee and to the Hydrogen Community as a whole. Dr. Kipperman was a very active member of our Agreement and brought a unique perspective to our view of how to achieve a hydrogen future. I particularly appreciated Dr. Kipperman's support during the last couple of years in his service as Vice-Chairman. We all wish Dr. Kipperman well in his retirement and thank him for his years of leadership and support.

I would again like to thank all of the Executive Committee members for their support and for their faith in my leadership. I welcome Mr. Trygve Riis of the Research Council of Norway as the new Chairman. My sincere thanks go to Ms. Elam for all of her hard work and support. She has been an integral part of our success. Finally, I would like to acknowledge the leadership of our Operating Agents and the dedication and contributions of our Task experts. All have made my time as Chairman extremely rewarding.

These are very important times for hydrogen technologies. All should be reminded of the importance of good planning, data collection and, above all, safety when carrying out any hydrogen research, development or demonstration project. All efforts will be closely scrutinized and the future potential for hydrogen will depend on reliable and reproducible results, established safety and reliability, and successful demonstration of technologies and system components. The entire hydrogen community must band together to ensure that we are putting the best foot forward and making the right choices to lead us towards a hydrogen future. The IEA Hydrogen Agreement is committed to providing leadership where it can, facilitating collaboration to accelerate technology development and peer review of technical results, provide tools that can help optimize and compare energy systems, and to disseminate technical information to the largest possible audience.

Life Cycle Assessments of Comparative Hydrogen Systems for Remote and Residential Applications

Pamela L. Spath, National Renewable Energy Laboratory, United States
Ronny Glöckner, Institute for Energy Technology, Norway
Arend de Groot, Energy Research Center of the Netherlands

[This report was written in support of Task 13, Design and Optimization of Integrated Systems, of the IEA Agreement on the Production and Utilization of Hydrogen. Task 13 completed its activities during 2001. The Final Report will be published during 2002 and will include the results of the studies discussed here, as well as the transportation system study and model development work that was conducted during this three-year collaboration.]

INTRODUCTION

Several studies involving modeling, economics, and environmental analysis are being performed under the auspices of the International Energy Agency Agreement on the Production and Utilization of Hydrogen Task 13, Design and Optimization of Integrated Systems. Specifically, life cycle assessments were performed for two different hydrogen applications: a remote system and a residential community. These studies are a joint effort led by the U.S. (life cycle assessment), Norway (remote system), and the Netherlands (residential community). For the remote system, the case examined involved the use of hydrogen in buses on a remote island off the coast of Norway. Two comparative systems were examined: (1) hydrogen is produced from wind/electrolysis and excess electricity is sent to the grid providing some power on the island; and (2) hydrogen is produced via a central steam methane reforming (SMR) plant, then a portion of the hydrogen is shipped to the remote island. For the residential community, the case studied was to provide heat and electricity to a district in the Netherlands. Again, two comparative systems were examined: (1) a central reformer produces hydrogen with a portion being supplied to the district where it is used in a proton exchange membrane fuel cell (PEMFC) to provide heat and power for each house (a small amount of electricity must also come from the grid and additional heat is provided by a heat pump); and (2) natural gas is burned in a boiler to supply heat and a natural gas combined cycle power generation system provides the electricity. Each system was examined in a cradle-to-grave manner and, therefore, includes all process steps necessary for operation, such as construction of the wind turbine, natural gas production and distribution, and transportation of the hydrogen.

CASE STUDY FOR A REMOTE SYSTEM

For this application, hydrogen production and storage are required in order to fuel three PEMFC buses. The resulting hydrogen requirement, based on the fuel consumption and driving range, is 32 kg/day of hydrogen. The modeling work, which was done by the Institute for Energy Technology (IFE Norway), examined several wind/electrolysis operating cases. For all of the cases examined, the size of the wind turbine was kept constant at 2 MW. In one case, the electrolyzer is operated at constant power to minimize the size of the electrolyzer. This means that at times power must be supplied from the grid when the wind resources are poor and some hydrogen storage is required. Two stand-alone scenarios were also examined where the

electrolyzer only operates when there are adequate wind resources. In one stand-alone case, referred to as the direct-connect scenario, the electrolyzer operates any time that the wind resources are adequate and the hydrogen storage is sized accordingly. The size of the electrolyzer and storage unit were determined by optimization calculations to achieve a design where the hydrogen storage is never entirely depleted, but there is adequate storage for periods of peak hydrogen production. For this case, the electrolyzer is operated at 80-100% of its maximum power 75% of the time and is idling 10% of the time. This resulted in an electrolyzer that is 48% greater and hydrogen storage that is 29 times larger than the constant power case. In the second stand-alone case, referred to as the top-charging scenario, the hydrogen storage is minimized and the operation of the electrolyzer is guided by the amount of hydrogen in the storage vessel. The electrolyzer is set to operate when the hydrogen storage reaches the lower dead-band limit and begins idling when the upper dead-band limit is reached. For this case, the electrolyzer operates near full power 30% of the time and is idling 60% of the time. The electrolyzer is not always operating when the wind resources are adequate, thus the electrolyzer must be larger than that for the direct-connect stand-alone scenario. For the top-charging stand-alone scenario, the electrolyzer is 248% greater and the hydrogen storage is 4 times larger than the constant power case. This means that the electrolyzer is 135% greater and the hydrogen storage is 85% less than the direct-connect stand-alone scenario. Considering both the economics (higher costs for the larger electrolyzers and storage units for the two stand alone cases) and the best operating practice, the most logical wind/electrolysis scenario for this situation is the constant power operation case, therefore, a life cycle assessment was done for this case only.

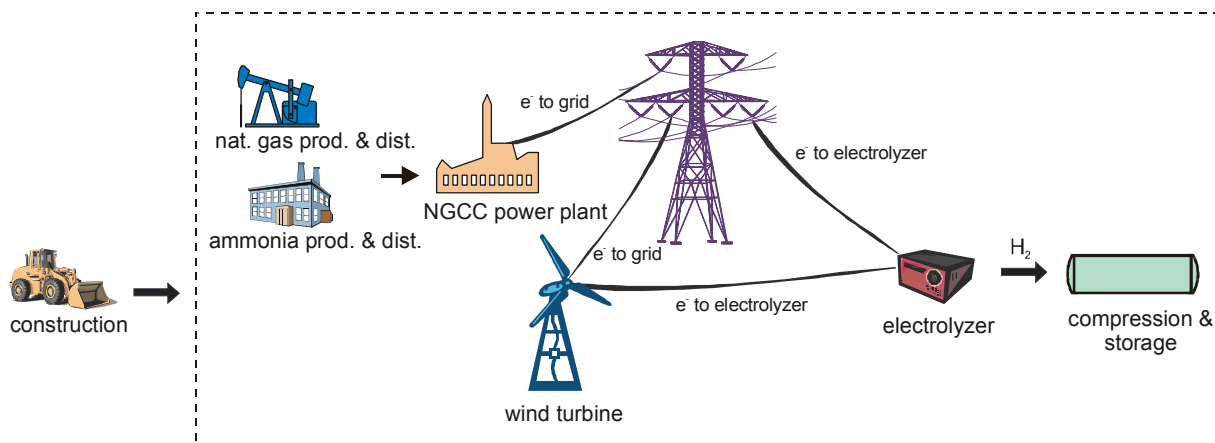
Because the wind turbine produces more electricity than is required for hydrogen production, the excess electricity is sent to the grid. At those times when the wind resources are poor, electricity is required from another source. Although the majority of Norway's electricity comes from hydro, new capacity is being generated from natural gas. Therefore, the electricity required during times of poor wind resources is assumed to come from a natural gas combined-cycle (NGCC) system via a sub sea cable. If the island were farther out in the ocean then the electricity would probably have come from diesel generators. Table 1 shows the electricity production and consumption of the wind/electrolysis system.

Table 1: Wind/electrolysis System Electricity Balance

| | Electricity produced or required (GJ/yr) |
|--|--|
| Total electricity produced by the wind turbine | 20,866 |
| Electricity required for hydrogen production and compression | 2,281 |
| Electricity required during times when wind resourced are poor | 308 |
| Excess electricity from wind turbine | 18,892 |

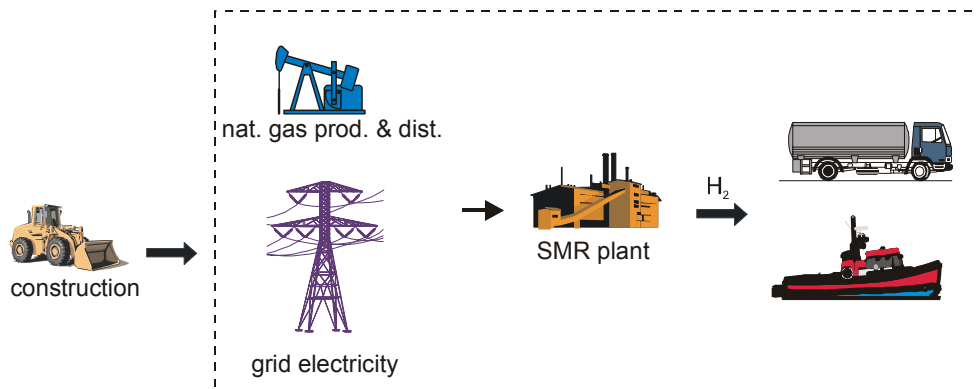
The graphic in Figure 1 shows the processes that make up this system.

Figure 1: Remote - Wind/electrolysis System



For comparison, a life cycle assessment was performed on a fossil based system - steam methane reforming (SMR). Hydrogen is assumed to be produced at a large central SMR plant then a portion of the hydrogen is compressed and shipped to the island in tube trailers over a distance of 100 km. Figure 2 shows the processes involved in hydrogen delivery from the SMR system.

Figure 2: Remote - SMR System



LCA RESULTS FOR REMOTE APPLICATION

Results of the remote system show that, in general, the resource requirement per kg of hydrogen is somewhat higher for the wind/electrolysis system than for the SMR system. This is due to the steel and concrete used in constructing the wind turbine. However, the air emissions and fossil energy consumption are lower for the wind/electrolysis system. Figure 3 compares the resource consumption of each system and Figure 4 compares the major air emissions. Note that, because of its magnitude, CO₂ is shown on a different scale. Table 2, which follows the graphs, gives the resource consumption, air emissions, global warming potential (GWP), solid waste generated, and energy consumption for both the wind/electrolysis system and the SMR system.

Figure 3: Remote Application - Comparison of Resource Requirements

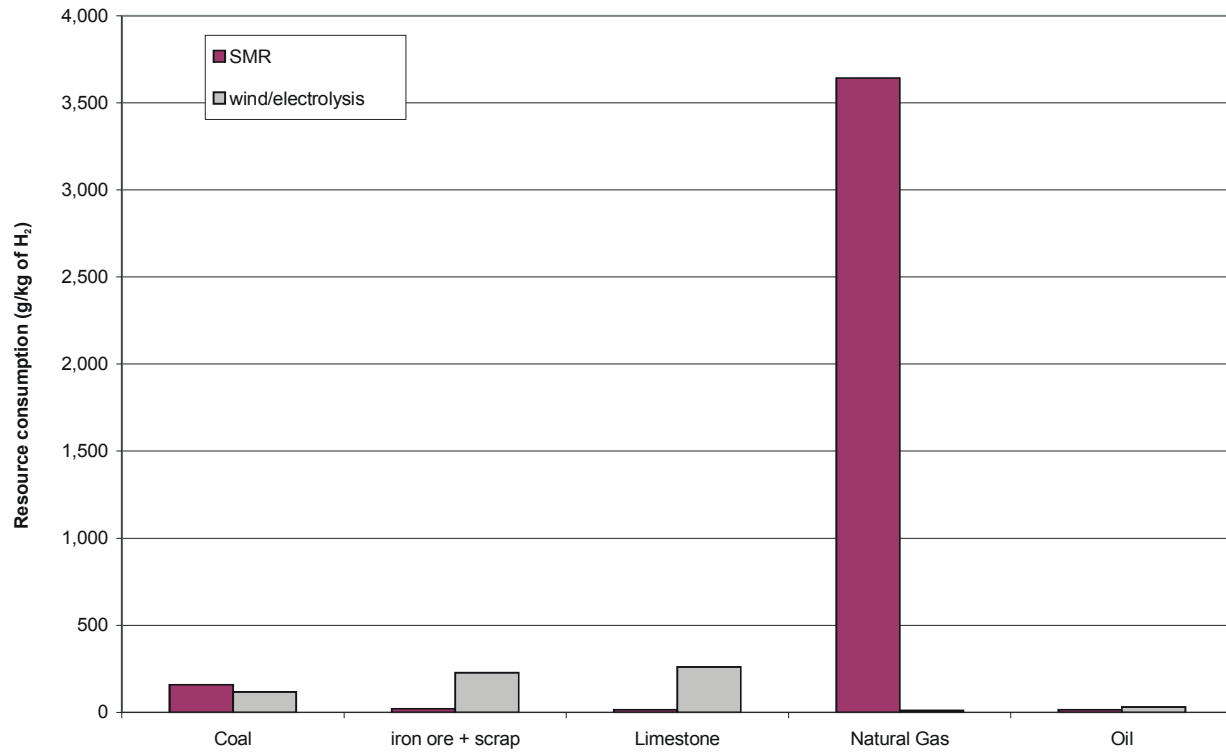


Figure 4: Remote Application - Comparison of Major Air Emissions Excluding CO₂

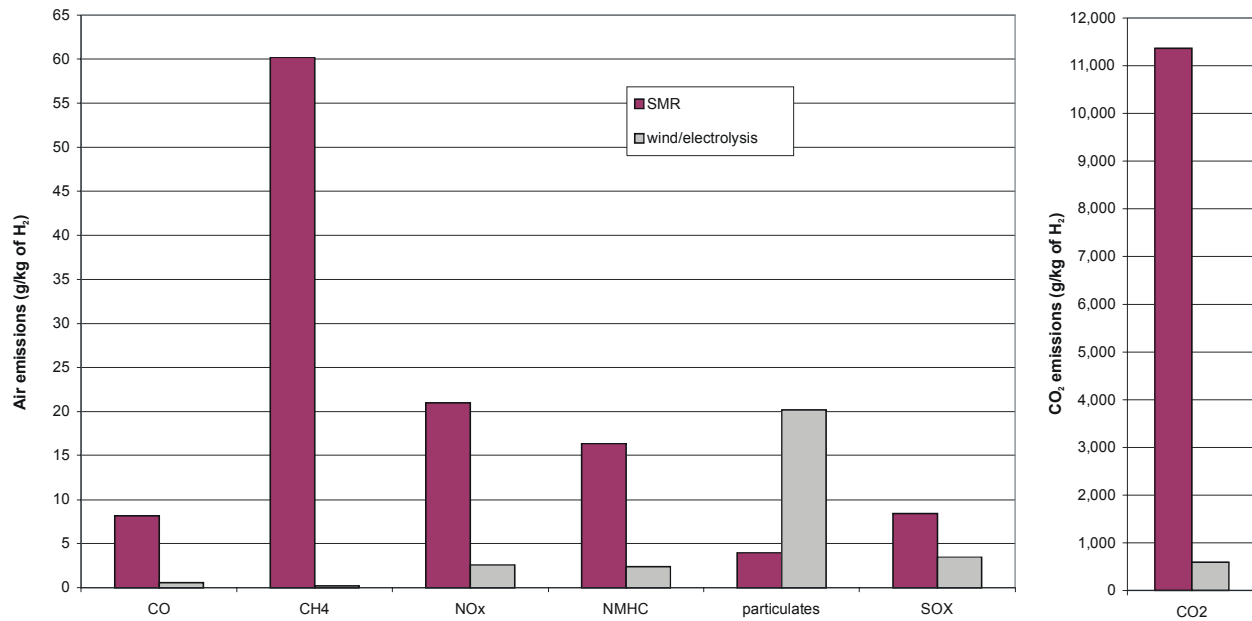


Table 2: Comparison of LCA Results for Remote Application

| | SMR | Wind/Electrolysis |
|--|---|---|
| Resource consumption | (g/kg of H₂) | (g/kg of H₂) |
| coal | 159 | 119 |
| iron (ore + scrap) | 21 | 227 |
| limestone | 16 | 261 |
| natural gas | 3,642 | 10 |
| oil | 16 | 31 |
| | (liters/kg of H₂) | (liters/kg of H₂) |
| Water consumption | 33 | 21 |
| AIR EMISSIONS | (g/kg of H₂) | (g/kg of H₂) |
| CO ₂ | 11,357 | 590 |
| CO | 8 | 0.6 |
| CH ₄ | 60 | 0.2 |
| NO _x | 21 | 3 |
| N ₂ O | 0.1 | 0.02 |
| NMHC | 16 | 2 |
| particulates | 4 | 20 |
| SO _x | 8 | 3 |
| | (g of CO₂-equivalent/kg of H₂) | (g of CO₂-equivalent/kg of H₂) |
| GWP (a) | 12,665 | 602 |
| % contribution from CO ₂ | 89.7% | 98.0% |
| % contribution from CH ₄ | 10.0% | 0.7% |
| % contribution from N ₂ O | 0.4% | 1.3% |
| | SMR | Wind/Electrolysis |
| Solid Waste | (g/kg of H₂) | (g/kg of H₂) |
| waste generated | 224 | 140 |
| Energy balance | (MJ/kg of H₂) | (MJ/kg of H₂) |
| total energy consumed | 195 | 5 |
| net energy ratio (E _{H₂} /E _{ff}) (b), (c) | 0.7 | 22 |
| external energy ratio (E _{H₂})/(E _{ff} - E _{ngfeed}) (c), (d) | 5 | N/A |

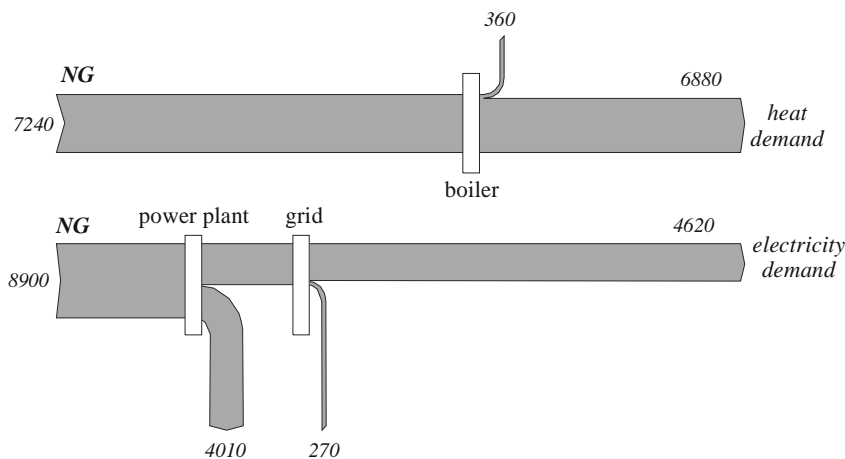
- (a) The GWP is considered to be a combination of CO₂, CH₄, and N₂O emissions. The capacity of CH₄ and N₂O to contribute to the warming of the atmosphere is 21 and 310 times higher than CO₂, respectively, for a 100-year time frame according to the Intergovernmental Panel on Climate Change (IPCC). Thus, the GWP of a system can be normalized to CO₂-equivalence to describe its overall contribution to global climate change.
- (b) This term illustrates how much hydrogen energy is produced for each unit of fossil fuel energy consumed.
- (c) E_{H₂} = the energy in the hydrogen produced; E_{ff} = the total fossil energy consumed by the system
- (d) E_{ngfeed} = the natural gas feedstock to the SMR plant; this term excludes the natural gas to the hydrogen plant indicating the fossil energy consumption from upstream processes.

As expected, the natural gas consumption per kg of hydrogen for the SMR system is considerably higher than that for the wind/electrolysis system. The air emissions show that the wind/electrolysis system has a considerable reduction in CO₂ and CH₄. Particulate emissions are higher for the wind/electrolysis system due to the concrete requirement; they come primarily from quarrying the sand and limestone needed for concrete production. The GWP is greatly affected by the use of natural gas, mostly because of the CO₂ emissions released during combustion and partly because of the CH₄ that is emitted to the atmosphere during natural gas production and distribution. The energy balance shows that the wind/electrolysis system produces 22 MJ of H₂ for every MJ of fossil energy consumed while the SMR system produces only 0.7 MJ of H₂ for every MJ of fossil energy consumed. The upstream energy consumption for the SMR system is high because, when the natural gas feedstock energy is excluded, the external energy ratio is still low. Also, note that the energy ratio for the SMR system is lower than the wind/electrolysis system even after subtracting out the energy content of the natural gas, 5 versus 22.

CASE STUDY FOR A RESIDENTIAL COMMUNITY

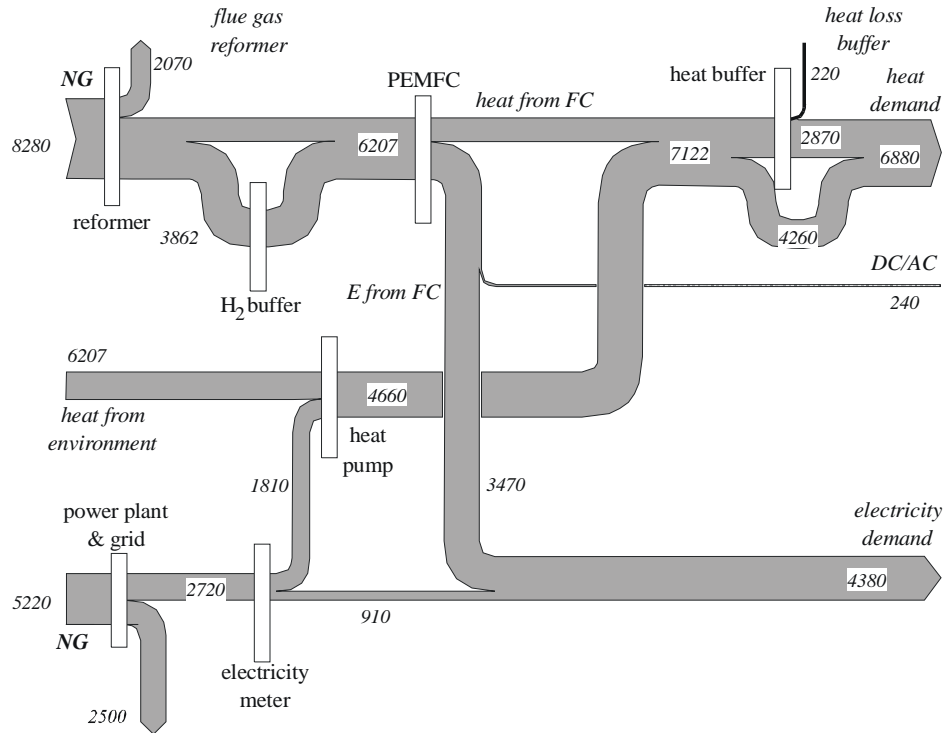
This application is to provide heat and electricity to a residential district in the Netherlands containing 1,300 houses. The heating and electricity requirement for the district is 6,880 MWh/yr and 4,380 MWh/yr, respectively. The Energy Research Centre of the Netherlands (ECN) did the modeling work for the residential application case. The conventional system uses a natural gas distribution system where heat is provided to each home by burning natural gas in a boiler and the electricity comes from a central natural gas combined-cycle plant. The Sankey diagram showing the district energy flow for this conventional system is shown in Figure 5. A life cycle assessment of this system was performed.

Figure 5: Sankey Diagram for Conventional Natural Gas System (Energy Flow in MWh/yr)



ECN examined several hydrogen distribution systems that integrated a combination of several of the following: PEM fuel cells, solid oxide fuel cells, heat pumps, natural gas burners, hydrogen burners, heat storage, and hydrogen storage. The hydrogen system chosen for the life cycle assessment work uses a 0.38 kW PEMFC integrated with a heat pump and hydrogen storage, along with make-up electricity from the grid. The Sankey diagram showing the district energy flow for this hydrogen network system is shown in Figure 6.

Figure 6: Sankey Diagram for Hydrogen System (Energy Flow in MWh/yr)



LCA Results for Residential Community

Figure 7 is a comparison of the resource consumption and Figure 8 is a comparison of the major air emissions for the conventional and hydrogen systems examined. Again, because of its magnitude, CO₂ is shown on a different scale. Except for natural gas, the hydrogen system consumes slightly more resources than the conventional system per kWh of heat and electricity supplied to the district. Because of the design and efficiency of the district heating and electricity production, the amount of natural gas required by the hydrogen system is less than that for the conventional system. The hydrogen system also produces less air emissions per kWh of heat and electricity supplied to the district.

The resource consumption, air emissions, GWP, solid waste generated, and energy balance for the each system are given in Table 3. The GWP of the hydrogen system is 16% less than that for the conventional system. The CH₄ emissions, primarily from natural gas production and distribution, contribute about 12% to the each system's GWP. The energy consumption of the conventional system is higher than the hydrogen system, 6.3 MJ/kWh of heat plus electricity compared to 4.9 MJ/kWh of heat plus electricity. The difference between the net energy ratio and external energy ratio indicates that the conventional system consumes considerably more upstream energy than the hydrogen system for every kWh of heat and electricity supplied to the district. There is also slightly less solid waste produced from the hydrogen system.

Figure 7: Residential Application - Comparison of Resource Requirements

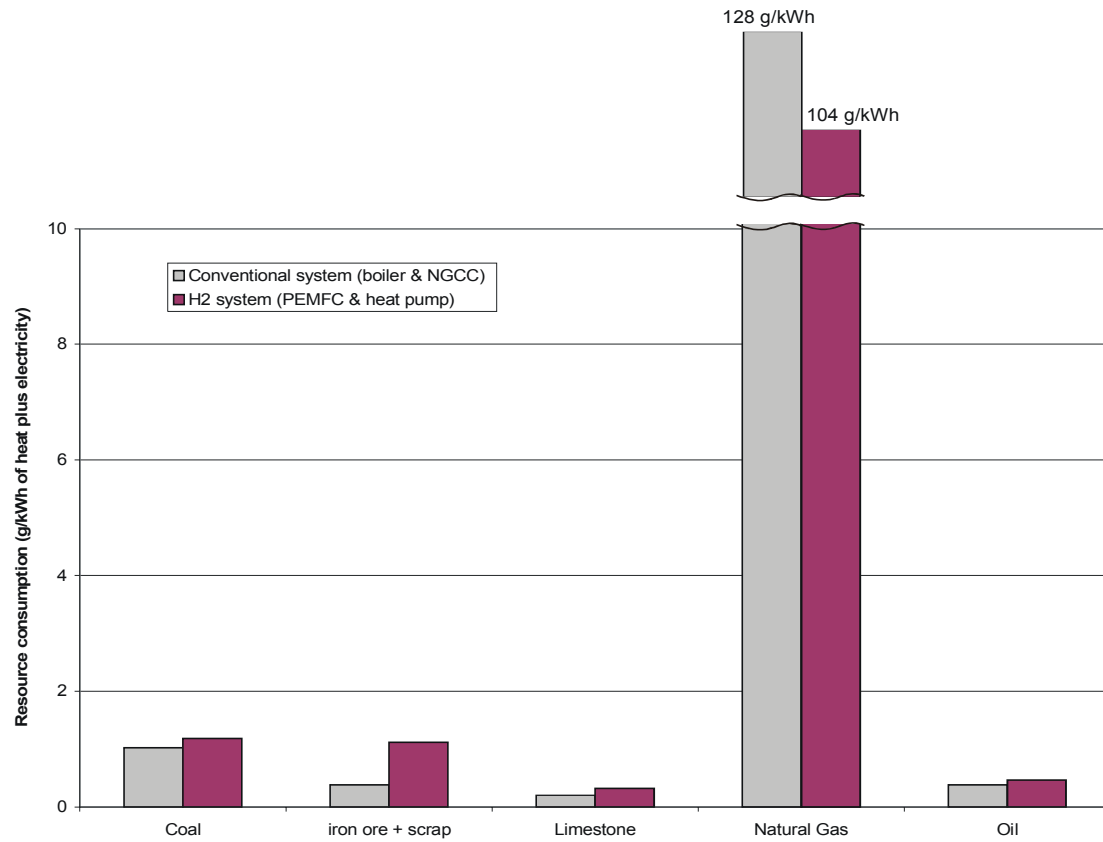


Figure 8: Residential Application - Comparison of Major Air Emissions (CO₂ is shown at the right)

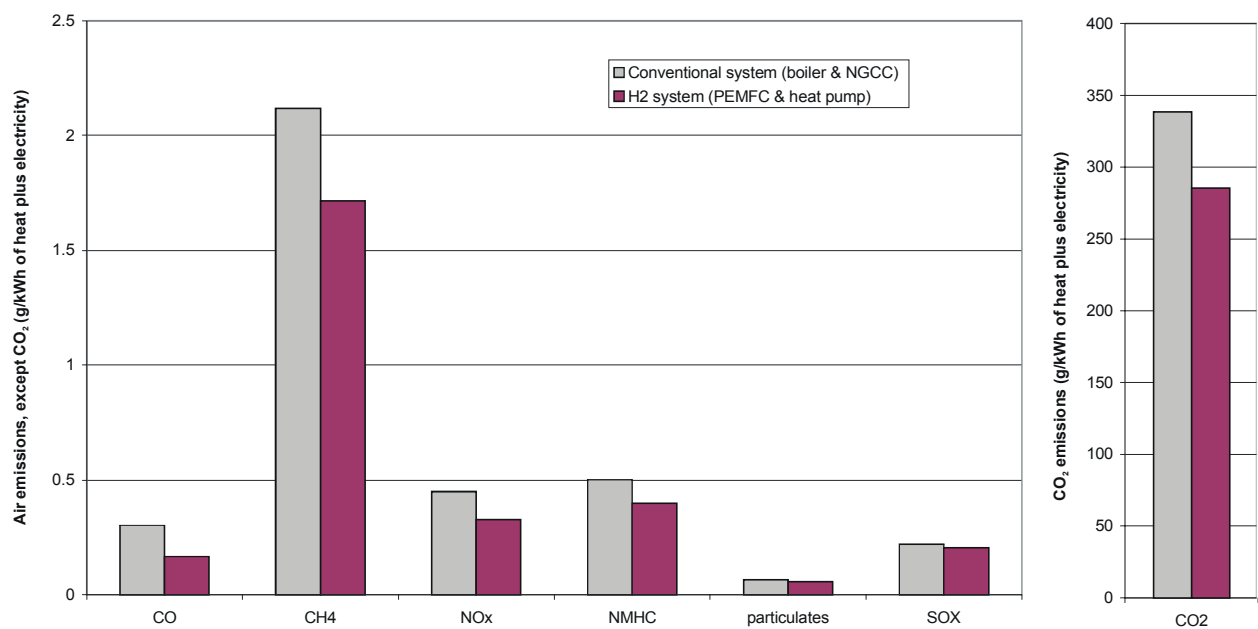


Table 3: Comparison of LCA Results for Residential Application

| | Conventional System (Boiler & NGCC) | Hydrogen System |
|--------------------------------------|--|--|
| Resource consumption | (g/kWh of heat plus electricity) | (g/kWh of heat plus electricity) |
| coal | 1.0 | 1.2 |
| iron (ore + scrap) | 0.4 | 1.1 |
| limestone | 0.2 | 0.3 |
| natural gas | 127.5 | 103.8 |
| oil | 0.4 | 0.5 |
| | (liters/kWh of heat plus electricity) | (liters/kWh of heat plus electricity) |
| Water consumption | 0.02 | 0.4 |
| | | |
| Air Emissions | (g/kWh of heat plus electricity) | (g/kWh of heat plus electricity) |
| CO ₂ | 338.5 | 285.4 |
| CO | 0.3 | 0.2 |
| CH ₄ | 2.1 | 1.7 |
| NO _x | 0.4 | 0.3 |
| N ₂ O | 0.0012 | 0.0006 |
| NMHC | 0.5 | 0.4 |
| particulates | 0.065 | 0.057 |
| SO _x | 0.22 | 0.20 |
| | Conventional System (Boiler & NGCC) | Hydrogen System |
| | (g of CO₂-equivalent/kWh of heat plus electricity) | (g of CO₂-equivalent/kWh of heat plus electricity) |
| GWP (a) | 383 | 322 |
| % contribution from CO ₂ | 88.3% | 88.7% |
| % contribution from CH ₄ | 11.6% | 11.2% |
| % contribution from N ₂ O | 0.1% | 0.1% |
| | | |
| Solid Waste | (g/kWh of heat plus electricity) | (g/kWh of heat plus electricity) |
| waste generated | 4.7 | 4.0 |
| | | |
| Energy balance | (MJ/kWh of heat plus electricity) | (MJ/kWh of heat plus electricity) |
| total energy consumed | 6.3 | 4.9 |
| | | |

| | Conventional System (Boiler & NGCC) | Hydrogen System |
|---|-------------------------------------|-----------------|
| life cycle efficiency ($E_{\text{dist}} - E_u - E_{\text{ng}}$)/(E_{ng}) (b), (c) | -53.8% | -29.6% |
| external energy efficiency ($E_{\text{dist}} - E_u$)/(E_{ng}) (c), (d) | 46.2% | 70.4% |
| net energy ratio (E_{dist})/(E_{ff}) (c), (e) | 0.6 | 0.7 |
| external energy ratio (E_{dist})/($E_{\text{ff}} - E_{\text{ng}}$) (c), (d) | 2.8 | 6.9 |

- (a) The GWP system is considered to be a combination of CO₂, CH₄, and N₂O emissions. The capacity of CH₄ and N₂O to contribute to the warming of the atmosphere is 21 and 310 times higher than CO₂, respectively, for a 100-year time frame according to the Intergovernmental Panel on Climate Change (IPCC). Thus, the GWP of a system can be normalized to CO₂-equivalence to describe its overall contribution to global climate change.
- (b) This efficiency includes the fossil energy consumption of all process steps in the system.
- (c) E_{dist} = electric and heat energy delivered to the district; E_u = energy consumed by the upstream processes; E_{ng} = energy contained in the natural gas to produce heat and power; E_{ff} = total fossil energy consumed within the system (i.e., $E_{\text{ff}} = E_u + E_{\text{ng}}$)
- (d) Excludes the natural gas to the hydrogen plant indicating the energy consumption from upstream processes.
- (e) This term illustrates how much electric and heat energy is delivered to the district for each unit of fossil fuel energy consumed.

SUMMARY AND RECOMMENDATIONS

For the remote application, in general, the renewable hydrogen system consumes more resources than the SMR system with the exception of the large amount of natural gas consumed by the SMR system. Apart from that, there is a considerable reduction in the air emissions, solid waste generated, and energy consumption by using wind/electrolysis. For the residential application, the resource consumption is higher for the hydrogen system compared to the conventional system. However, the air emissions, energy consumption, and solid waste generated are somewhat less for the hydrogen system. The hydrogen system in the residential application is fossil based, but if this system were to use hydrogen produced from a renewable source, then the air emissions, especially CO₂ and CH₄, and the energy consumption, will be even lower. The economics of these systems are being examined by Norway and the Netherlands. Putting this information together with the LCA results will give the cost of avoided emissions, waste, and energy consumption for the novel versus conventional system. This is especially important for the residential application to determine if the small savings in emissions, waste, and energy consumption merit the anticipated higher cost of the hydrogen system. Additionally, in terms of the residential application, if the central SMR plant were located close to the district and some of the steam from this hydrogen production facility were available, a scenario where steam is used instead of additional heat from a heat pump should be examined.

HYDROGEN ENERGY ACTIVITIES IN THE UNITED KINGDOM

Ray Eaton

Department of Trade and Industry, UK

Barry Lakeman

Defence Science and Technology Laboratory, UK

[We are pleased to welcome the United Kingdom back into the IEA Agreement on the Production and Utilization of Hydrogen. The following are highlights of some of the important hydrogen-related activities currently underway in the UK.]

INTRODUCTION

In order to slow the rate of global climate change, the Kyoto summit targeted significant reductions in global greenhouse gas emissions. One method of achieving such reductions is through the increased deployment of renewable energy. The UK has imposed an obligation on electricity suppliers to deliver 10% of electricity from designated renewable energy sources by 2010, a significant increase from the present level of about 2%. Additional support measures include increased funding for the Department of Trade and Industry's New and Renewable Energy Programme and the introduction of grants to support the deployment of specific technologies, such as offshore wind and photovoltaics. The Government is currently considering the possibility of further targets for renewable energy deployment beyond 2010. An Energy White Paper is expected to be published before the end of 2002.

Transport has a potentially significant role to play in reducing greenhouse gas emissions and on 31 July 2002 the Government published "Powering Future Vehicles – The Government Strategy". The objective is that the UK should lead the global shift to clean, low carbon transport. Key elements in the strategy are the adoption of targets for low and ultra low carbon vehicles and the formation of a Low Carbon Vehicles Partnership.

While many experts argue that the long-term goal should be the adoption of a global hydrogen economy, there are many techno-economic issues that would need to be solved before this vision could become a reality. However, the long transition phase to the Hydrogen Economy, say 30 to 50 years, means that the UK is well placed to make a significant contribution to addressing the issues, and participation in the IEA Agreement is one of the important mechanisms for doing so.

This paper briefly summarizes ongoing hydrogen activities in the UK in three broad areas: Government-led initiatives, research in academic institutions, and activities in commercial and non-academic organizations. It concentrates on the research-based initiatives that have been on going throughout the period of this Annual report.

UK GOVERNMENT INITIATIVES

Renewable Energy Programme

The UK government has a goal to reduce carbon dioxide emissions and is investigating various clean energy technologies to achieve this. One element of the Government's policy is the Renewable Energy Programme. The budget for this has increased significantly in recent years (£10.6M in 1999/00, £14M in 2000/01, £18M in 2001/02). The principal role of the programme is to support innovation by industry that has the prospect of improving the competitiveness of new and renewable energy. This is achieved through funding for R & D projects. Studies are also undertaken to help guide the programme, inform the development of policy and identify issues that may affect the deployment of renewable energy. In addition, the Programme undertakes technology transfer and promotional activities to disseminate results and raise awareness of renewable energy.

The Renewable Energy Programme is currently looking to support projects in the following areas:

- Biofuels
- Photovoltaics
- Offshore Wind
- Wave
- Tidal Stream
- Fuel Cells
- Embedded Generation
- Hydro

Hydrogen is not featured as a separate sub-programme, but hydrogen-related work has been supported under the Fuel Cells Programme. A review of Government Energy R&D by the Chief Scientific Advisor recommended that there should be a separate programme for hydrogen and the Powering Future Vehicles Strategy announced the Government's intention of establishing a Hydrogen and Low Carbon Fuels Programme.

Environmental and Physical Sciences Research Council (EPSRC)

The EPSRC is one of the research councils that administer government funding for academic research at universities. The EPSRC portfolio of hydrogen research covers a diverse range of topics, from fuel cells and materials to storage and the hydrogen economy, with a current value of approximately £2M. Projects are distributed throughout the Chemistry, Physics, Materials and Engineering Programmes. The major item in the portfolio is the Sustainable Power Generation and Supply Initiative, SUPERGEN, which operates within the Engineering Programme. The other major project is the Hydrogen Network.

- SUPERGEN

Four initial SUPERGEN consortia have been formed to carry out this work: Marine (mainly wave power); Networks (electricity supply and distribution systems); Biomass (thermal methods for generating power from biomass); and Sustainable Hydrogen Technologies.

The Sustainable Hydrogen Technologies consortium comprises six university partners: Bath (Chemical Engineering), Birmingham (Chemistry and Materials), Queen Mary and Westfield College-University of London (Materials), Nottingham (Materials and Chemistry) and Glamorgan (Technology).

The main theme of the consortium is sustainable hydrogen storage (using solid state methods) and generation. Funds of up to £2M GBP have been made available for the consortium for a four-year programme starting in Spring 2003. Additional funds are being sought from industrial and non-academic research partners, who will be expected to provide engineering and design input to the work.

- H2NET

The aim of this UK Hydrogen Energy Network (H2NET) is to promote the development of hydrogen-based energy systems by creating a forum where research priorities can be discussed and members can develop research and development collaborations. The network, which has well over a 100 members from UK industry and academics, also aims to identify technical and infrastructural barriers to the exploitation of hydrogen as a fuel stock, and to develop appropriate strategy documents.

H2NET will consider all aspects of hydrogen utilization from gas production, through storage, to end-use applications, and the important over-arching topics of safety, economics, and system design.

The inaugural meeting was held at Rutherford Appleton Laboratory on 12 July 2000. More than 30 academics, industrialists and representatives of public bodies interested in the development of a hydrogen energy economy attended the meeting. Since then, there have been further workshops on hydrogen-related issues and the membership has increased significantly.

ACADEMIC RESEARCH

Many UK universities are undertaking research into a number of issues associated with hydrogen and fuel cells. A major source of UK Government funding for universities is administered through the various research councils, of which the EPSRC is the major player in the hydrogen arena. Highlights from work at a few key universities will be briefly described, followed by a brief summary of work being undertaken at other academic establishments.

Bath University - Hydrogen Storage in Carbon Materials *Dr Tim Mays, Chemical and Materials Engineering*

The central theme of this work is to measure, understand and predict hydrogen adsorption isotherms on carbon materials. The main tool for measurement is gravimetry. The Department currently has a new Hiden IGA system capable of measuring kinetic and equilibrium adsorption isotherms up to 20 bar, and from cryogenic to furnace temperatures.

In 2002, a Sartorius gravimetric adsorption system donated by the Royal Military College, Kingston, Ontario, Canada, is to be commissioned. This unit will be able to measure isotherms up to 150 bar. Adsorption/desorption isotherms are being measured for pure and ultra-pure

hydrogen on a range of carbons materials including carbon nanotubes and nanofibres, and on active carbons made using a wide variety of precursors and methods.

The objectives of this work are to map out the loadings (wt.% H₂), temperatures and pressures for different materials, and to determine the conditions for maximum loading/storage. Analytical models are being developed to represent the data. Molecular simulations of hydrogen adsorption on carbons, using density functional theory and Monte Carlo methods, are also being undertaken. These will aid in the understanding of measured isotherms, the development of models, and the design of materials for optimal hydrogen storage capacity.

Glamorgan University - Bio-Hydrogen Production
Dennis Hawkes, School of Technology

Using glucose as a substrate and with nitrogen sparging, microorganisms have been utilized in a 10 liter, continuous fermentation reactor to produce approximately 0.2 liters of hydrogen per liter of reactor per hour and at a retention time of 8.5 hours. With starch (using a co-product from production of food-grade wheat starch), similar rates have been obtained and the problem of long term, continuous production is now being addressed. Utilization of energy crops will also be studied.

Nottingham University - Enhancing the Hydrogen Storage Capacity of Carbon Nanofibres
Gavin Walker, Advanced Materials, School of Mechanical, Materials, Manufacturing Engineering and Management

The overall aim of this proposed project will be to modify the surface of carbon nanofibres in order to enhance the hydrogen storage capacity for these materials. The project has three major objectives:

- i. Remove amorphous carbon and thus improve hydrogen storage;
- ii. Remove caps over graphite layers, thus opening up more planes for hydrogen sorption; and
- iii. Control the surface chemistry of carbon nanofibres to maximize hydrogen storage.

The project will be concerned with the synthesis of targeted carbon nanofibres (using standard preparations), the surface modification of these carbon nanofibres, surface characterization, hydrogen storage measurements, and the correlation of hydrogen storage capacity with surface characteristics.

Other projects from Nottingham University include:

- Hydrogen storage using carbon whiskers - John Patrick, Advanced Materials, School of Mechanical, Materials, Manufacturing Engineering and Management. The work is funded by Air Products.
- Novel concepts for small-scale gasification of biomass/waste, in particular the use of microwave heating to generate synthesis gas from which hydrogen can be separated - Sam Kingman and Colin Snape, School of Mechanical Engineering and Mine Engineering. The project is departmentally funded.

Queen Mary and Westfield College, University of London - Modeling and Processing of New Hydrogen Storage Materials
Xiao Guo, Department of Materials

The aim of this effort is to develop high performance hydrides, with a high hydrogen-storage capacity, high kinetics for hydrogen release, a low dissociation temperature, and a moderate dissociation pressure, that are light weight and low cost. The major challenge is to produce one material system that meets all of the above requirements. Combined statistical, theoretical, and novel experimental approaches are being used to understand and enhance the essential hydrogen storage properties of selected hydrides, including: Mg-, C-, NaAl-, and NaB- based materials.

Current Research:

Artificial Neural Network (ANN) Modeling of Compositional/Microstructural Effects: ANN modeling is a relatively new simulation technique of synthesizing an existing database and predicting unapparent relationships, in this case composition/microstructure with hydrogen storage properties, by making intelligent use of past research findings. Both Mg and LaNi₅ systems are being simulated.

Alloy stability is being evaluated from the calculation of the electronic structure and binding energy using the first principles, full potential, linearized, augmented plane wave (FLAPW) method. Hydrogen desorption pressure and temperature can then be determined by the Van't Hoff equation. The fundamental issues of surface and surface curvature effects on the mechanism and extent of physisorption and/or chemisorption of hydrogen will then be determined from binding energy and electronic density calculations. Curved nanostructures with a capillary width less than a few molecular diameters (i.e. 1-2 nanometers) have overlapping potential fields from opposite walls so that the attractive force acting on hydrogen is greater than on an open flat surface. Well-tested first principles codes, e.g., WIEN-2K and CASTEP, will be used to estimate the formation enthalpy of both alloys and their corresponding hydrides and to investigate the influence of alloy site substitutions on the intrinsic hydrogen-storage properties.

Experimental Solutions to the Next-Generation Hydrogen Storage Materials/Systems: Chemical alloying of Mg and MgH₂ with desirable elements predicted by the above theoretical analyses is being undertaken using a high energy ball mill within a high-pressure hydrogen atmosphere, in order to produce fine, nanostructured powder for storage characterizations. An electrolysis coating technique is used to modify powder surface properties for easy activation. Hydrogen capacity, dehydrogenation kinetics and cycle life will be evaluated by thermogravimetry and Pressure-Composition-Temperature isotherms.

Salford University - Hydrogen Storage
Keith Ross, Institute for Materials Research

Salford is studying the absorption isotherms for hydrogen in single-walled carbon nanotubes at low temperatures using a computer-controlled microbalance. A nanotube production facility has also been established in order to determine how variations in the production conditions affect the properties of the tubes formed and good quality material is being produced. The geometry of samples of nanotubes is assessed using low angle X-ray diffraction, yielding the diameter of the tubes and the number of tubes in each "rope".

Work on in situ neutron diffraction studies of the hydrogen-absorption/desorption cycling behavior of AB₅ materials used in metal hydride batteries is also being undertaken. The

diffraction line-broadening phenomenon is being utilized to develop a method of studying the processes involved.

Neutron scattering has been demonstrated to be a very powerful tool for studying hydrogen storage systems. Measurements on nanotubes show the molecular rotation of hydrogen molecules, and this information is being used to determine the sites for hydrogen uptake.

An extensive experimental study of hydrogen in the prototype Laves phase compound ZrV_2 was recently completed. Neutron techniques were used to study the diffusion mechanism and Monte Carlo techniques were used to model the macroscopic consequences of this model. This work is now being extended to ab initio modeling that, in principle, will allow the screening of the vast number of Laves phase compounds for appropriate properties. This approach can also be extended to other classes of compounds.

Hydrogen-related research undertaken in other academic institutions is summarized below.

University of Birmingham: Metal hydrides for hydrogen storage, solid oxide fuel cells, reforming.

Cambridge University: Carbon nano-structures for hydrogen storage.

Cranfield University: Low cost polymer electrolyte membranes, both acid and alkali.

Edinburgh University: Solid oxide fuel cells, reforming catalysts.

Glasgow University: Sulfur-tolerant reforming catalysts.

Heriot-Watt University: Biological hydrogen production.

Imperial College London: Studies on the technical, economic and politic impact of hydrogen/fuel cells, solid oxide fuel cells, catalysts and membranes, direct methanol fuel cells, turbines.

Kings College, London: Biological hydrogen production.

Loughborough University: Fuel cells research.

Newcastle University: Direct methanol fuel cells, both acid and alkali.

Open University: Fuel cell catalysts.

Oxford University: Carbon nanostructures for hydrogen storage, biofuel cells using hydrogen and the hydrogenase enzyme.

Rutherford and Appleton Laboratory: H₂NET administration, storage systems for renewable energy sources, hydrogen's role in reducing greenhouse gases.

St Andrews University: Reforming catalysts, solid oxide fuel cells, high temperature proton conductors.

Salford University: Carbon nanotubes for hydrogen storage.

Southampton University: Biofuel cells, fuel cell catalyst studies.

Strathclyde University: Carbon nanostructures and metal hydrides for hydrogen storage.

University of Surrey: Membrane electrolytes and fuel cells.

UMIST: Solid oxide fuel cells, reforming catalysts, high temperature proton conductors.

COMMERCIAL AND NON-ACADEMIC ORGANISATIONS

A number of UK companies and other institutions have an interest in hydrogen. These are summarized below.

Air Products (UK): Production and distribution of hydrogen, hydrogen safety.

Birmingham University: Microbiological hydrogen production and hydrogen storage in metal alloys, special zeolites, carbons, and other porous structures.

BOC (UK): Production and distribution of hydrogen.

BP Amoco: Natural gas and methanol reformation, vehicle-refueling infrastructures, electrolysis, participants in the Clean Urban Transport for Europe (CUTE) EU project.

Dstl: Hydrogen storage, reformation, fuel cell development.

EA Technology: Fuel cells and reformation processes.

H2SPC Ltd: Hydrogen production from the direct photolysis of water.

Ineos Chlor Ltd: Fuel cell bipolar plates, corrosion-resistant metal coatings for bipolar plates, electrolyzers.

Innogy Technology Ventures Ltd: Hydrogen production from natural gas using bromine, fuel cells for domestic power, polymer electrolyte membranes.

Intelligent Energy: Fuel cell design, reformation and fuel cell production for portable power and home power generation.

Johnson Matthey: Fuel cell and reformer catalysts, reforming of methanol (and other hydrocarbons), gas clean up, membrane electrode assembly production, reversible hydrogen storage in metal alloys, collaborating with Birmingham University on the FUSCHIA EU-funded project for automobiles.

Microponents: Fuel cell bipolar plate development and manufacture.

Morgan Materials Technology Ltd: Carbon materials for fuel cell applications, including bipolar plates.

QinetiQ: Hydrogen storage, reformation, fuel cell development, carbon nanofibres for hydrogen storage.

Rolls Royce: Solid oxide fuel cells and reformer technologies.

Scottish and Southern Energy Plc: Fuel cells and hydrogen fuel.

Shell Global Solutions: New refueling technologies, safety, and hydrogen storage, involved in the Iceland hydrogen economy project.

Southwest Electrolysers: Fleet buses using internal combustion engines and hydrogen derived from wind power for the county of Cornwall.

Synetix: Catalysts for reformation.

Wellman Defence: Hydrocarbon reforming technologies and electrolyzers.

Whitby Bird & Partners: Urban generation of hydrogen from sunlight (USHER project).

SUMMARY

The UK has a strong research and development skill base that can be focused on the needs of hydrogen research. In particular, there are certain technology gaps that UK industry and academia could address in order to make a significant contribution to global hydrogen research. These include:

- Fast, safe refueling technologies
- Novel, compact hydrogen storage methods
- Low cost, emission-free hydrocarbon reforming/cracking technologies
- Gas clean-up technologies
- Efficient, low cost, compact compressors for hydrogen and air
- High pressure electrolyzers
- Reversible fuel cells
- Biological hydrogen production and gas clean-up, building on the UK expertise in gene manipulation and immobilized enzymes
- Photo-electrolysis

HYDROGEN FROM BIOMASS – STATE OF THE ART AND RESEARCH CHALLENGES

Thomas A. Milne, Carolyn C. Elam and Robert J. Evans
National Renewable Energy Laboratory

[The following is the Executive Summary of the IEA Technical Report, “Hydrogen from Biomass – State of the Art and Research Challenges.” This report was prepared in support of development efforts for the new IEA Hydrogen Agreement Task 16, Hydrogen from Carbon Containing Materials. The full report can be found on the IEA Hydrogen Agreement Web site at <http://www.eren.doe.gov/hydrogen/iea>. Task 16 will begin work during 2002.]

Executive Summary

Approximately 95% of the hydrogen produced today comes from carbonaceous raw material, primarily fossil in origin. Only a fraction of this hydrogen is currently used for energy purposes; the bulk serves as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries. However, hydrogen's share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Hydrogen production will need to keep pace with this growing market.

In the near term, increased production will likely be met by conventional technologies, such as natural gas reforming. In these processes, the carbon is converted to CO₂ and released to the atmosphere. However, with the growing concern about global climate change, alternatives to the atmospheric release of CO₂ are being investigated. Sequestration of the CO₂ is an option that could provide a viable near-term solution.

Reducing the demand on fossil resources remains a significant concern for many nations. Renewable-based processes like solar- or wind-driven electrolysis and photobiological water splitting hold great promise for clean hydrogen production; however, advances must still be made before these technologies can be economically competitive. For the near- and mid-term, generating hydrogen from biomass may be the more practical and viable, renewable and potentially carbon-neutral (or even carbon-negative in conjunction with sequestration) option. Recently, the International Energy Agency's (IEA) Program on the Production and Utilization of Hydrogen launched its new Task 16, Hydrogen from Carbon-Containing Materials, to bring together international experts to investigate some of these near- and mid-term options for producing hydrogen with reduced environmental impacts. In addition to large-scale fossil-based production with carbon sequestration and production from biomass, small-scale reforming for distributed generation is included in the activity.

This review of the state of the art of hydrogen production from biomass was prepared to facilitate in the planning of work that should be done to achieve the goal of near-term hydrogen energy systems. We describe the relevant technologies that convert biomass to hydrogen, with emphasis on thermochemical routes. In evaluating the viability of the conversion routes, each must be put in the context of the availability of appropriate feedstocks and deployment scenarios that match hydrogen to the local markets. Co-production opportunities are of particular interest for near-term deployment since multiple products improve the economics; however, co-product development is not covered in this report.

We do not discuss the nature of the biomass feedstock, but any economically viable process must be closely linked to the characteristics of the locally available materials and appropriately sized for the supply. Relevant feedstock qualities are: cost, distribution, mass, physical and chemical characteristics. All of these qualities must be considered when matching feedstock with conversion technology. Biomass feedstocks vary greatly in both composition and form. Both moisture and energy content are key parameters in the evaluation of biomass and also lead to a number of engineering considerations that must be addressed. Since biomass is low in density, the transportation costs for both the feedstock and the hydrogen must be balanced with the savings from employing economy of scale. The distribution of hydrogen production sites requires a decision on the transport of both the biomass and the hydrogen. These characteristics will make it difficult to compete with natural gas steam reforming without credits and has inhibited the implementation of commercial biomass systems to date.

The first task in biomass hydrogen development is to identify the optimum match of feedstock, production technology, and end-use options. Techno-economic comparisons are the only way to make rational selection of appropriate R&D paths in this complex and rich technical area. Regional perspectives will vary greatly and, hence, opportunities will be different for Europe, N. America, Asia, and the developing regions of the world. These items are not reviewed here, but they must guide the identification of R,D&D needs (a selection of recent references is given below). (See IEA Bioenergy Task 35, Techno-economic assessments for Bioenergy Applications.)

Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Since biomass is renewable and consumes atmospheric CO₂ during growth, it can have a small net CO₂ impact compared to fossil fuels. However, hydrogen from biomass has major challenges. There are no completed technology demonstrations. The yield of hydrogen is low from biomass since the hydrogen content in biomass is low to begin with (approximately 6% versus 25% for methane) and the energy content is low due to the 40% oxygen content of biomass. Since over half the hydrogen from biomass comes for the spitting of water in the steam reforming reaction, the energy content of the feedstock is an inherent limitation of the process. The yield of hydrogen as a function of oxygen content is shown in Figure 1. The low yield of hydrogen on a weight basis is misleading since the energy conversion efficiency is high. For example, the steam reforming of bio-oil at 825°C with a five-fold excess of steam demonstrated in the laboratory has an energy efficiency of 56%.

However, the cost for growing, harvesting and transporting biomass is high. Thus, even with reasonable energy efficiencies, it is not presently economically competitive with natural gas steam reforming for stand-alone hydrogen without the advantage of high-value co-products. Additionally, as with all sources of hydrogen, production from biomass will require appropriate hydrogen storage and utilization systems to be developed and deployed.

Biomass conversion technologies can be divided into two categories: 1) direct production routes and 2) conversion of storable intermediates. Direct routes have the advantage of simplicity. Indirect routes have additional production steps, but have an advantage in that there can be distributed production of the intermediates, minimizing the transportation costs of the biomass. The intermediates can then be shipped to a central, larger-scale hydrogen production facility. Both classes have thermochemical and biological routes. Figure 2 shows the technologies that are reviewed in this report.

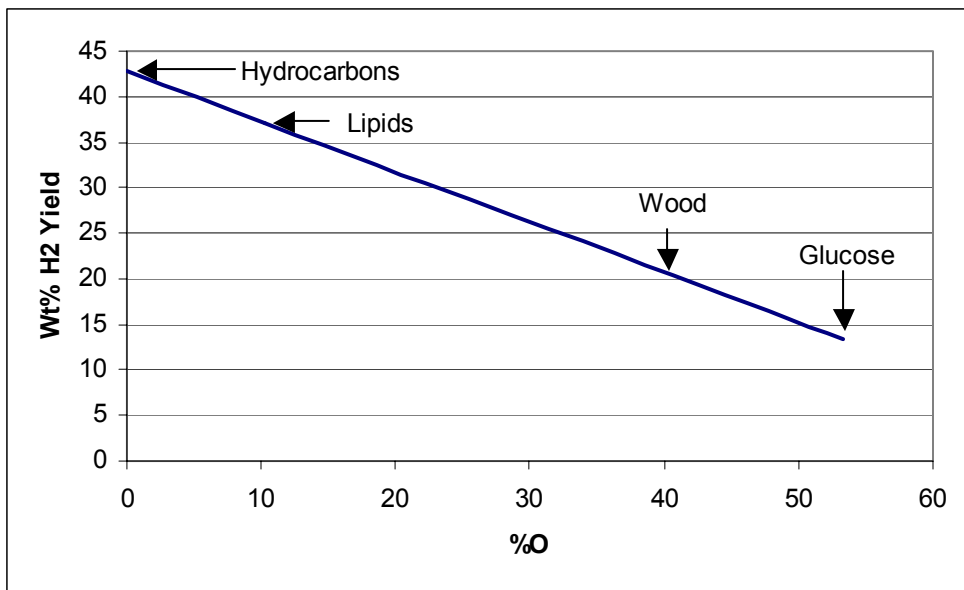


Figure 1. Theoretical yield of H₂ as a function of feed composition

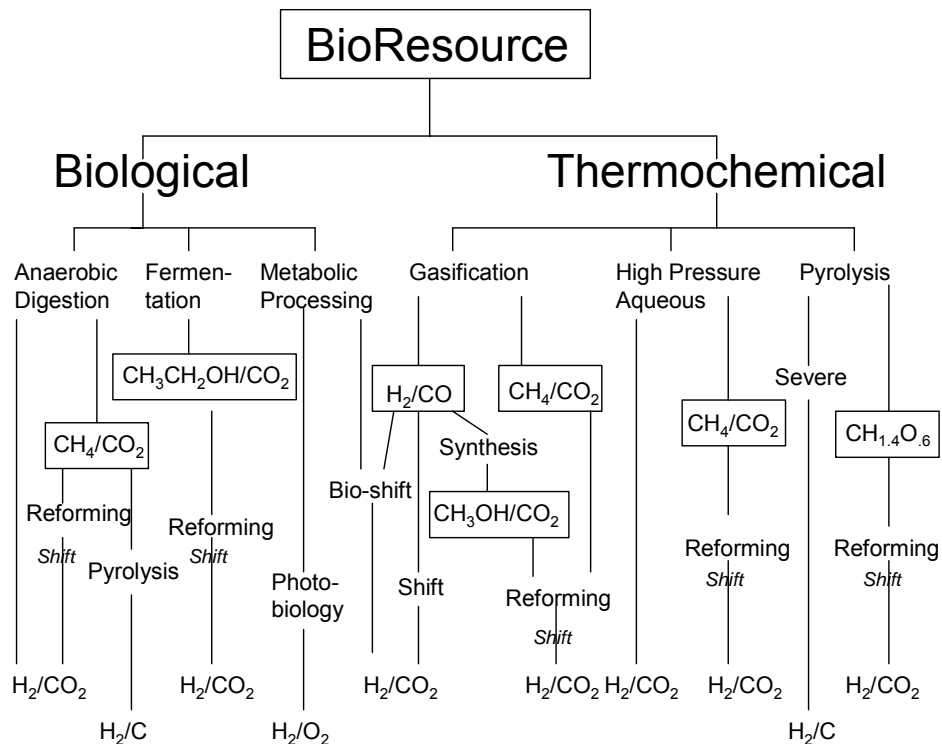


Figure 2. Pathways from Biomass to Hydrogen - storable intermediates are shown in boxes.

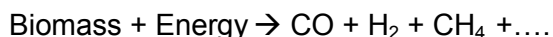
A third aspect of biomass is metabolic processing to split water via photosynthesis or to perform the shift reaction by photo biological organisms. The photo-biological production of hydrogen is only briefly cited since it is an area of long-term research that is outside the scope of biomass conversion and is covered in a separate IEA Task. The use of microorganisms to perform the shift reaction is of great relevance to hydrogen production because of the potential to reduce carbon monoxide levels in the product gas far below the level attained using water gas shift catalysts and, hence, eliminate final CO scrubbing for fuel cell applications. The following serves as an introduction to the areas reviewed in this report.

Direct Production of Hydrogen from Biomass

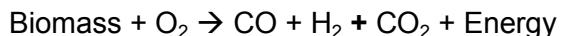
Gasification is a two-step process in which a solid fuel (biomass or coal) is thermochemically converted into a low- or medium-Btu gas. In the first reaction, pyrolysis, the dissociated and volatile components of the fuel are vaporized at temperatures as low as 600°C (1100°F). Included in the volatile vapors are hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar, and water vapor. Because biomass fuels tend to have more volatile components (70-86% on a dry basis) than coal (30%), pyrolysis plays a larger role in biomass gasification than in coal gasification. Gas phase thermal cracking of the volatiles occurs, reducing the levels of tar. Char (fixed carbon) and ash are the pyrolysis by-products that are not vaporized. In the second step, the char is gasified through reactions with oxygen, steam, and hydrogen. Some of the unburned char may be combusted to release the heat needed for the endothermic pyrolysis reactions.

Gasification coupled with water-gas shift is the most widely practiced process route for biomass to hydrogen. Thermal, steam and partial oxidation gasification technologies are under development around the world. Feedstocks include both dedicated crops and agricultural and forest product residues of hardwood, softwood and herbaceous species.

Thermal gasification is essentially high severity pyrolysis although steam is generally present. An example of this is the Sylvagas (BCL/FERCO) low-pressure, indirectly heated circulating fluid bed.

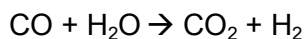


By including oxygen in the reaction gas the separate supply of energy is not required, but the product gas is diluted with CO₂ and, if air is used to provide the oxygen, then nitrogen is also present. Examples of this are the GTI (formerly IGT) High-Pressure Oxygen-Blown Gasifier, as well as the circulating fluid bed by TPS Termiska.



Other relevant gasifier types are bubbling fluid beds being tested by Enerkem, and the high-pressure high-temperature slurry-fed entrained flow Texaco gasifier.

All of these gasifier examples will need to include significant gas conditioning, including the removal of tars and inorganic impurities and the conversion of CO to hydrogen by the water-gas shift reaction:

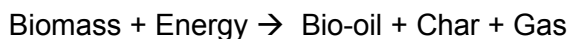


Significant attention has been given to the conversion of wet feedstocks by high-pressure aqueous systems. This includes the supercritical-gasification-in-water approach by Antal and coworkers as well as the supercritical partial oxidation approach by General Atomic. Pyrolysis to hydrogen and carbon is being explored as a viable technology for carbon sequestration although most work is applied to natural gas pyrolysis. Biomass or biomass-derived intermediates could be processed in this way.

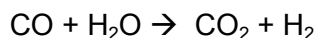
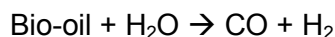
Biological conversion via anaerobic digestion is currently being practiced by workers around the world resulting in methane that can be processed to hydrogen by conventional steam reforming processes.

Storable Intermediates

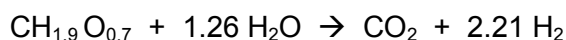
Pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of fuels, chemicals and materials. The reaction is endothermic:



The oil can be formed in 66 wt.% yield. Chornet and coworkers have developed the concept of using the residual fractions of the oil for hydrogen after co-products have been produced. Catalytic steam reforming of Bio-oil at 750-850°C over a nickel-based catalyst is a two-step process that includes the shift reaction:



The overall stoichiometry gives a maximum yield of 17.2 g H/100 g bio-oil (11.2% based on wood).



Regional networks of pyrolysis plants could be established to provide oil to a central steam reforming facility. The process is compatible with other organic waste streams such as aqueous-steam fractionation processes used for ethanol production and trap grease. Methanol and ethanol can also be produced from biomass by a variety of technologies and used for on-board reforming for transportation. Methane from anaerobic digestion could be reformed along with natural gas. Methane could be pyrolyzed to H₂ and C if markets for carbon black were available

Systems analysis has shown that biomass gasification / shift conversion is economically unfavorable compared to Natural Gas Steam Reforming (NGSR) except for very low cost biomass and potential environmental incentives. The pyrolysis with valuable co-product approach yields hydrogen in the price range of \$6 - \$8/GJ, which is promising for near term applications.

Promising areas for biomass to hydrogen conversion technology R,D&D are determined by the range of available low cost biomass feedstocks and the markets for hydrogen in areas where the feedstocks are available. The major areas for R,D&D are:

- **Feedstock preparation and feeding.** For biological routes, pretreatment to increase accessibility is an issue, and for thermochemical routes, there are major issues for the preparation of the variety and nature of the feeds for high temperature and pressure reactors.
- **Gasification gas conditioning.** The key to hydrogen utilization is fuel cell applications and so product purity requirements for the fuel cell will drive the gas purity requirements of all production systems. In gasification, the presence of hydrocarbons and trace levels of nitrogen, sulfur, and chlorine compounds must be addressed, not only for end use applications, but also for shift reaction catalysts and separation systems, such as pressure swing adsorption.
- **System integration.** The development of hydrogen technology depends on the integration of several key steps that must be practiced at appropriate scales of operation. Technical and economic analysis is required to match the optimum technology with available feedstock to produce a product of the necessary quality for the target application. Although biomass to hydrogen allows great flexibility in deployment, it also means a greater array of technical possibilities must be covered.
- **Modular systems development.** There is an opportunity for biomass systems to address small-scale and remote opportunities. These systems will require novel conversion and gas conditioning technologies and will also need to be designed appropriately for the resources and technical expertise available in that region.
- **Valuable co-product integration.** Appropriate systems for conversion of by-product streams from chemical and biological processing of biomass are the best prospects for near-term development.
- **Larger-scale demonstrations.** The most promising technologies will need to be selected at the larger-scale. These demonstrations will need to include successful utilization of the hydrogen (i.e. in a fuel cell, internal combustion engine, turbine, etc).

These are in addition to the challenges for any hydrogen process in storage and utilization technologies.

The technologies reviewed in this report will be discussed by international experts using the following criteria:

- Technical feasibility
- Interest of the participating countries
- Feedstock availability
- Potential use for the hydrogen
- Economic potential

Those identified by the experts as the most promising will be the subject of further review and/or research under the new IEA Hydrogen Agreement Task 16, Hydrogen from Carbon Containing Materials. Techno-economic and life cycle analyses will be performed on select technologies in the context of regional perspectives and to identify opportunities for further R,D&D.

REVIEW OF SMALL STATIONARY REFORMERS FOR HYDROGEN PRODUCTION

Joan M. Ogden
Princeton University

[The following is the Executive Summary of the IEA Technical Report, "Review of Small Stationary Reformers for Hydrogen Production." This report was prepared in support of development efforts for the new IEA Hydrogen Agreement Task 16, Hydrogen from Carbon Containing Materials. The full report can be found on the IEA Hydrogen Agreement Web site at <http://www.eren.doe.gov/hydrogen/iea>. Task 16 will begin work during 2002.]

EXECUTIVE SUMMARY

Approximately 95% of the hydrogen produced today comes from carbonaceous raw material, primarily fossil in origin. Only a fraction of this hydrogen is currently used for energy purposes; the bulk serves as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries. However, hydrogen's share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Hydrogen production will need to keep pace with this growing market.

In the near term, increased production will likely be met by conventional technologies, such as natural gas reforming. In these processes, the carbon is converted to CO₂ and released to the atmosphere. However, with the growing concern about global climate change, alternatives to the atmospheric release of CO₂ are being investigated. Sequestration of the CO₂ is an option that could provide a viable near-term solution.

Cost of building sufficient distribution infrastructure and transporting hydrogen over large distances are major economic barriers to the implementation of hydrogen-based technologies, particularly in the transportation sector. Additionally, large-scale central production will depend on market volumes to evolve in order to compensate for the capital expenditures of building up capacity. Thus, distributed production via smaller reformer systems is viewed as an attractive near- to mid-term option for supplying hydrogen, particularly for vehicles and in regions where low-cost natural gas is readily available, and for securing market share for hydrogen technologies.

Reformer technology is commercially available today. However, scale economies in capital cost can be significant. Lower pressure and temperature and lower cost materials are needed to make small-scale, distributed reforming competitive. Minimizing CO₂ emissions must also be addressed, as carbon capture and sequestration will be too costly at the small scale.

Recently, the International Energy Agency's (IEA) Program on the Production and Utilization of Hydrogen launched its new Task 16, Hydrogen from Carbon-Containing Materials, to bring together international experts to investigate some of these near- and mid-term options for producing hydrogen with reduced environmental impacts. In addition to large-scale fossil-based production with carbon sequestration, small-scale reforming for distributed generation and technologies to convert biomass to hydrogen are included in the activity.

This review of current hydrogen production technologies was prepared to facilitate in the planning of collaborative activities to be carried out under the auspices of the IEA and focusing on advancing small-scale reformers for distributed hydrogen production. This report surveys conventional technologies:

- Steam Methane Reforming
- Partial Oxidation
- Auto-Thermal Reforming
- Methanol Reforming
- Catalytic Cracking of Methane
- Ammonia Cracking

Novel reformer technologies, such as sorbent enhanced reforming, ion transport reforming, plasma reforming and microchannel reforming are also discussed. Technologies are reviewed based on performance characteristics, development status, economics and research issues for small-scale units.

As a result of this survey, the following have been concluded:

- Industry, government and academic researchers from fuel cell, hydrogen and energy producing communities need to identify and prioritize specific issues facing small-scale reformers for producing hydrogen for given applications and resources.
- Market assessment and system studies should be conducted to evaluate reformer technologies for both distributed and centralized hydrogen production, and for refueling station design.

Through the IEA, international experts will be brought together to further discuss these and other issues facing widespread implementation of small-scale reformer technology, particularly for transportation markets.

TASK 13 – DESIGN AND OPTIMIZATION OF INTEGRATED SYSTEMS

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Operating Agent for the
United States Department of Energy

Introduction

Hydrogen energy systems have been proposed as a means to increase energy independence, improve domestic economies, and reduce greenhouse gas and other harmful emissions from stationary and mobile sources. These systems, however, face technical and economic barriers that must be overcome before hydrogen can become a competitive energy carrier for the 21st century. In an effort supported by the International Energy Agency Hydrogen Agreement (Annex 11 - Integrated Systems), design guidelines were developed for a large number of hydrogen-based and non-hydrogen-based components. These guidelines provide data on individual components to assist in the design of integrated energy systems. Included in the guidelines are measures of performance that provide relevant means to compare systems. In addition, a tool was developed to assist in the design of hydrogen energy systems. Computer models were developed for a large number of hydrogen production, storage, distribution, and end-use technologies, based on data collected from hydrogen demonstration projects throughout the world. These models can be linked through the use of a common integrating platform into integrated hydrogen systems. Renewable-based and fossil-based components are included in the component model library to assist in comparative analysis between advanced systems and commercial systems.

Objective

The objective of Task 13 was to provide a means to increase energy independence, improve domestic economies, and reduce greenhouse gas and other harmful emissions from stationary and mobile sources. Emphasis was placed on comparison of systems with respect to efficiency, environmental impact, capital and operating costs, and other measures of importance.

To accomplish this objective, work was performed within the framework of two coordinated Subtasks.

Duration

The Task began on 1 January 1999 and was completed 31 December 2001.

Participation

Participants in Task 13 were: Canada, European Commission, Japan, Lithuania, the Netherlands, Norway, Spain, Sweden, Switzerland and the United States.

Task Description and Progress

- **Subtask A: Model Development**

Subtask A included improvement to existing component models and development of additional component models (Activity A1), and the development of cost models for each component model (Activity A2). The results of this Subtask supported the analyses that were performed in Subtask B.

Activity A1: Component Model Development and Improvement

In the evaluation of existing and proposed hydrogen demonstration systems, it may be necessary to develop additional component models in order to perform technical and cost analyses. A more robust pressure swing adsorption model that can operate as a stand-alone model (rather than as an integral part of several of the current models) was developed as part of this activity.

Documentation of the new or revised models followed the standard format established in Annex 11.

Activity A2: Cost Model Development

The basis for the development of consistent cost models was established and includes appropriate size ranges, scaling factors, installation factors, operating and maintenance costs, etc. This basis was used throughout this activity to insure consistency and fairness. Cost models based on existing non-proprietary data and standard-engineering procedures were developed. This activity included development of spreadsheet models. A range of sizes was identified for the components, so that the cost models would be applicable for a range of integrated system sizes. These cost models include non-proprietary projections for future costs based on cost-reduction parameters (such as mass production, market size, and technological advances) that were defined as part of this activity (based on literature values to the largest extent possible).

- **Subtask B: Systems Analysis**

Subtask B activities involved the identification of candidate configurations (in cooperation with Subtask A), design of the system using the design guidelines developed in Annex 11, modeling of the integrated systems using the tool developed in Annex 11, and evaluation of the performance, costs and environmental benefits of hydrogen energy systems.

Experts canvassed potential hydrogen demonstration project leaders in participant and non-participant countries to identify candidate configurations for analysis. Using information, tools, and methodologies developed in Annex 11, comparison of different system configurations for a particular application could be made. This required a set of criteria on which the comparison could be made, including efficiency, environmental impacts, economic impact, capital and operating costs, and other measures of importance to the analyst. In all cases, these parameters can be reduced to a comparison of costs, given that appropriate value can be assigned to the individual criteria. Three case studies were selected for evaluation.

Residential Systems

The Team Leader for this system was the Netherlands; the United States performed the Life Cycle Assessment (LCA).

The development of greenfield communities is an important opportunity for hydrogen energy systems. In the Netherlands, new residential districts are being developed, with housing additions of 60,000 (1-2% of the total housing market of 6 million). There is an ambitious national plan to require the power generation mix to include 3% renewables (green energy) by 2010 and 10% renewables by 2020. The Dutch national energy policy includes price supports via an eco-tax of up to 30% on non-green energy. Given the requirement to integrate renewables in the national power mix, continued deregulation of utilities, and the desires by many communities to include “green” homes, hydrogen systems offer interesting opportunities for residential developments.

Introducing hydrogen as an energy carrier requires a different infrastructure from the existing infrastructure. Developing such an infrastructure for mobile applications is a much-debated issue. For stationary applications, the role of hydrogen is less defined, but will likely depend strongly on the introduction strategies for fuel cells. The first large-scale application of fuel cells may well be small-scale combined heat and power (CHP) systems. One interesting starting point for developing a hydrogen infrastructure is the use of hydrogen as a fuel for CHP units based on fuel cells. To fully realize the ultimate clean-energy benefits, hydrogen energy systems will use hydrogen from renewable sources. However, in the nearer term, hydrogen will most likely be produced from fossil fuels. The availability of appropriate technologies to support a hydrogen energy system based on fossil fuels is one important aspect of this early-introduction strategy.

An integrated systems approach was used to design the energy system for a new community or district. Services required included heating, lighting, communications, etc. Technologies considered included PEM fuel cells, solid oxide fuel cells, heat pumps, combined heat and power (CHP), heat buffer, electric grid, natural gas grid, hydrogen grid, etc. Schematics of the four main configurations examined in the Residential Systems study are shown in Figure 1.

Using Matlab, systems were designed using cost, efficiency, and environmental impacts as Measures of Performance. The results of the simulations indicated that the size of the buffer was influenced by and also influenced the size of the components and the use of the grids (for storage and as an energy supplier).

Introducing hydrogen as an energy carrier requires a different infrastructure from the existing infrastructure. For stationary applications, the role of hydrogen will likely depend strongly on the introduction strategies for fuel cells. The first large-scale application of fuel cells may well be small-scale CHP systems. One interesting starting point for developing a hydrogen infrastructure is the use of hydrogen as a fuel for CHP units based on fuel cells. To fully realize the ultimate clean-energy benefits, hydrogen energy systems will use hydrogen from renewable sources. However, in the nearer term, hydrogen will most likely be produced from fossil fuels. The availability of appropriate technologies to support a hydrogen energy system based on fossil fuels is one important aspect of this early-introduction strategy.

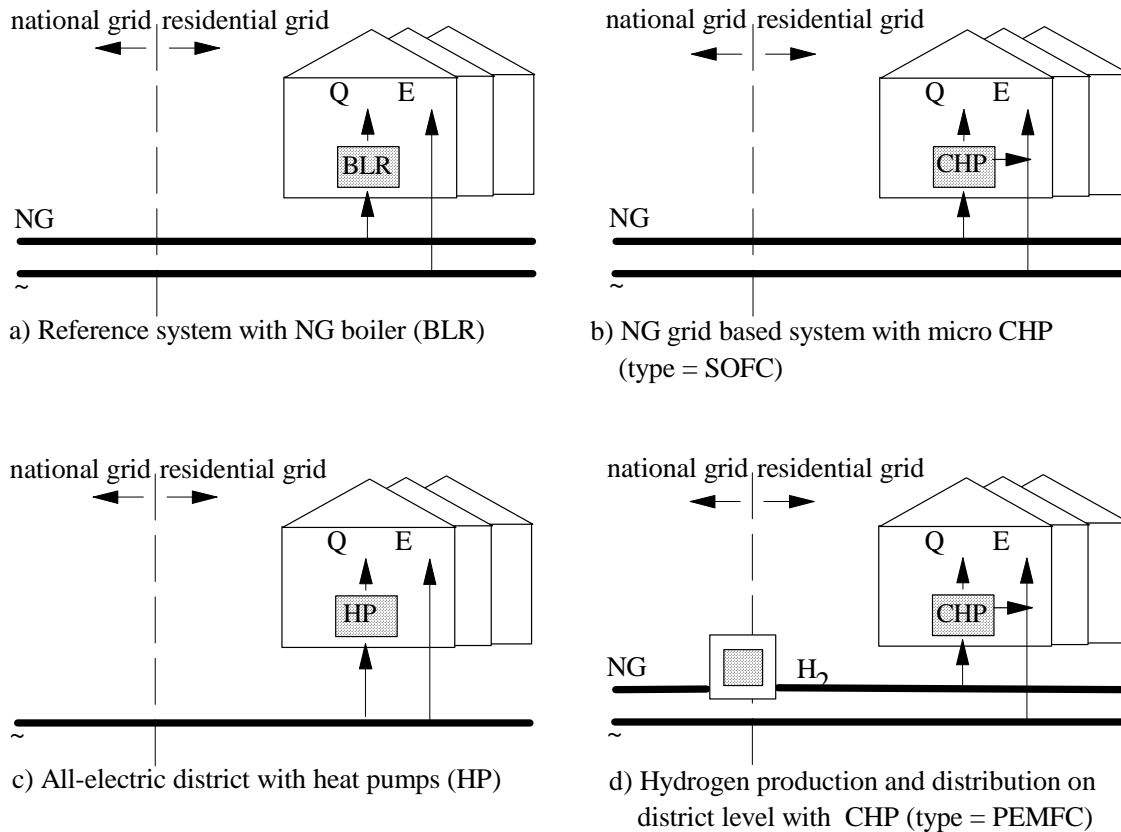


Figure 1 - Configurations for supplying heat and electricity to households in the Residential System study.

Remote Communities

The Team Leader for this system was Norway; the U.S. performed the LCA.

Hydrogen energy systems have been proposed as a means to increase energy independence, improve domestic economies, and reduce greenhouse gas and other harmful emissions from stationary and mobile sources. These systems, however, face technical and economic barriers that must be overcome before hydrogen can become a competitive energy carrier for the 21st century. A wind-H₂ system for a remote location was studied to determine the feasibility of producing hydrogen for transportation applications.

In Norway, more than 99% of the electricity demand is supplied by hydropower. During the last 10 years, however, public resistance based on environmental issues has virtually brought the development of the remainder of these resources to a standstill. Because of the increase in power demand and good wind resources along a sparsely populated coastline (a potential of around 10 TWh/year is recognised), the focus on wind energy plants has grown over the last years. It seems that the public resistance, especially in the early phase of the introduction of large-scale wind energy development, is smaller than is the case for further hydropower

development. Over the last year (2000), the Norwegian government has approved several applications for building of wind parks, in total amounting to some 300 MW peak power.

The selected locations for Norwegian wind parks are remote areas, such as islands, where the best wind resources are found. The wind parks will produce power for the small communities in these areas, but also for the common electricity grid as a complement to the existing hydropower. In this study, the production and use of hydrogen in fuel cells in relation to such wind parks was reviewed. A wind/electrolyzer-based hydrogen refueling station taking the base power from one of the large windmills in a wind park was studied. The hydrogen produced was assumed to be used in buses operating the public transport on the remote location. At a later stage, hydrogen for operation of ferries would also be an attractive alternative.

For this application, hydrogen production and storage were required in order to fuel three PEMFC buses. The resulting hydrogen requirement based on the fuel consumption and driving range was 32 kg/day of hydrogen. For all of the cases examined, the size of the wind turbine was kept constant at 2 MW, since this is the size of the actual turbines in the existing wind farm. In one case, the electrolyzer is operated at constant power to minimize the size of the electrolyzer. This means that at times power must be supplied from the grid when the wind resources are poor and some hydrogen storage is required. Two stand-alone scenarios were also examined where the electrolyzer only operates when there are adequate wind resources. In one stand-alone case, referred to as the direct-connect scenario, the electrolyzer operates any time that the wind resources are adequate and the hydrogen storage is sized accordingly. The size of the electrolyzer and storage unit were determined by optimization calculations to achieve a design where the hydrogen storage is never entirely depleted but there is adequate storage for periods of peak hydrogen production. For this case, the electrolyzer is operated at 80-100% of its maximum power 75% of the time and is idling 10% of the time. This resulted in an electrolyzer that is 48% greater and hydrogen storage that is 29 times larger than the constant power case. In the second stand-alone case, referred to as the top-charging scenario, the hydrogen storage is minimized and the operation of the electrolyzer is guided by the amount of hydrogen in the storage vessel. The electrolyzer is set to operate when the hydrogen storage reaches the lower dead-band limit and begins idling when the upper dead-band limit is reached. For this case, the electrolyzer operates near full power 30% of the time and is idling 60% of the time. The electrolyzer is not always operating when the wind resources are adequate, thus the electrolyzer must be larger than that for the direct-connect stand-alone scenario. For the top-charging stand-alone scenario, the electrolyzer is 248% greater and the hydrogen storage is 4 times larger than the constant power case. This means that the electrolyzer is 135% greater and the hydrogen storage is 85% less than the direct-connect stand-alone scenario. Considering both the economics (higher costs for the larger electrolyzers and storage units for the two stand alone cases) and the best operating practice, the most logical wind/electrolysis scenario for this situation was the constant power operation case, therefore, a life cycle assessment was done for this case only.

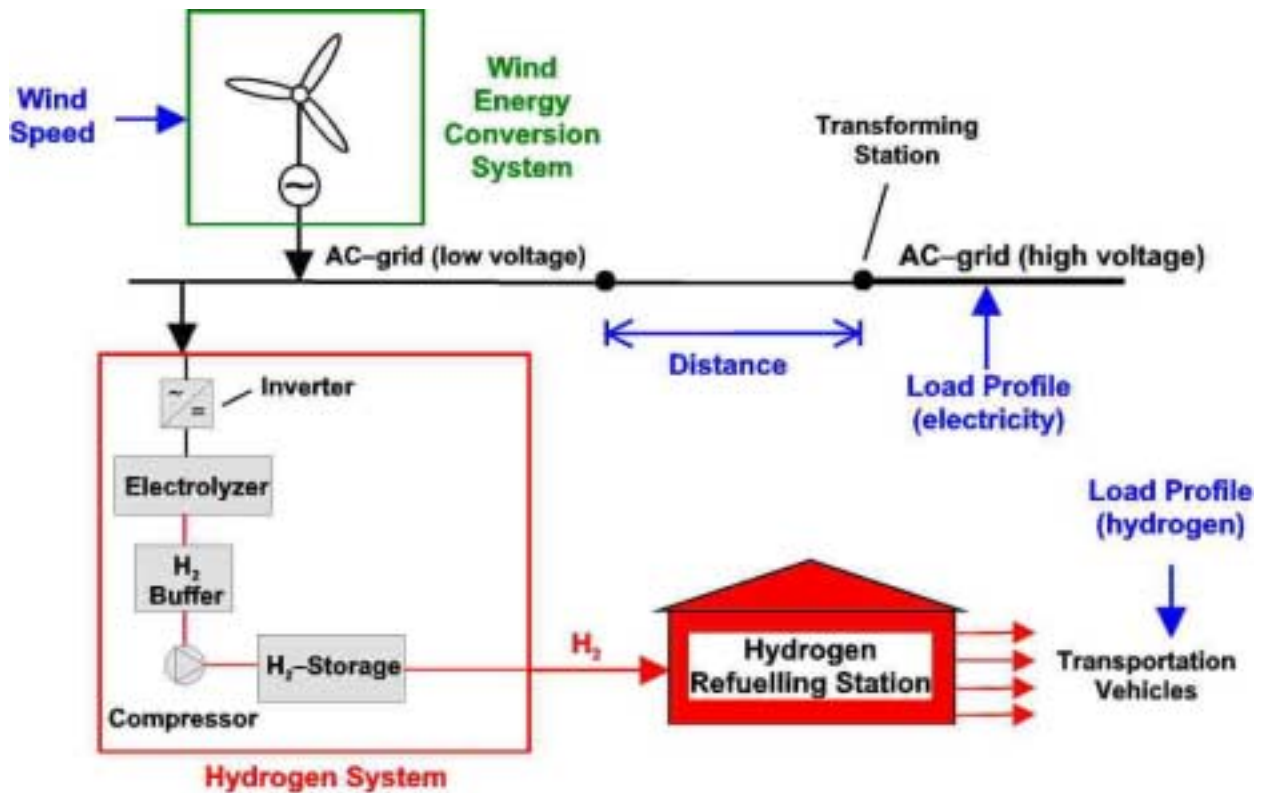


Figure 2 - Schematic of the Remote Communities system under study.

Transportation System

The Team Leader for this system was the U.S.; Switzerland and the European Commission performed LCAs.

The goal of the Transportation Systems case study was to address specific hydrogen demonstration opportunities with respect to energy independence, improved domestic economies, and reduced emissions. The transportation analysis was not as geographically specific as the other two case studies. The overall scope of the analysis included comparison of hydrogen passenger vehicle fueling options including refueling alternatives (primarily various sources of liquid and gaseous hydrogen), vehicle configuration alternatives (primarily various hydrogen storage and power plant configurations), drive cycle implications, and cost variations (electricity, natural gas, and hydrogen).

Efforts during this period were focused on the end use of various infrastructure alternatives, specifically:

- Fuel economy estimates for various hydrogen vehicles and alternative vehicles
- Tailpipe emissions of various vehicle configurations
- Station/local emissions for various station and vehicle combinations

The objective was to aid decision-making with respect to vehicle and station type, thus guiding infrastructure development.

The fuel economy analysis was based primarily on other estimates, i.e., estimates from other sources are summarized and compared. Major sources were recent DTI studies [1,2] and current PSI results [3]. Some parameters that were considered in an attempt to find consistency among the studies were: vehicle weight, vehicle driving range, and driving cycle. The type of power plant, type of storage system, and the fuel type impact vehicle weight. As an example, for a base case vehicle weight of 900 kg, each additional kg of storage weight contributes 1.5 kg of vehicle weight. [1]

Emissions results were also based primarily on other studies. These were also surveyed and compared. To help illustrate the local environmental impact, tailpipe and station emissions were estimated independently, although it was difficult in some studies to separate fueling operations emissions from the total.

For the methanol and gasoline fueled vehicles, results were based on previous work by Ogden [4] and The American Methanol Foundation [5]. Methanol and gasoline stations were assumed to be similar to the hydrogen station, i.e., same vehicle refueling capacity and same typical urban location. The methanol and gasoline storage tanks were assumed to be filled by weekly truck delivery, as in the hydrogen case. The diesel delivery trucks and the delivery process contribute to the local pollution; EPA data were used to estimate this impact.

A number of initial assumptions were made regarding operation of the transportation and refueling system. These were applied to the cost and sizing analysis of the station. Specifically for hydrogen refueling these assumptions include:

- Only passenger vehicles are currently under consideration.
- The base case calls for capacity to refuel 100 vehicles per day.
- Each vehicle-refueling event requires approximately 4 kg of hydrogen. As a result, at 100% utilization, 400 kg hydrogen is served per day. Storage is sized to serve the entire anticipated volume of customers, plus a buffer, as described below.
- A refueling station consists of the hydrogen production unit or receiving area, storage and its associated facilities, and the dispensing area with two dispensing units. These are the capital cost components considered in this study.
- Available dispensing hours are 24 hours per day, 365 days per year.
- On-site hydrogen production capacity is sized to fill the required storage once per day (a trade-off between production capacity or rating and operating hours was considered for the electrolyzer and UOB cases to minimize the combined capital cost and electricity cost).
- Liquid delivery is scheduled once per week. An average round trip delivery distance of 1500 miles was assumed. The dewar is sized for one week's service plus 30%, to maintain proper conditions and reduce boil-off in the tank.
- Compressed gas storage capacity is oversized by 40% to maintain adequate pressure for dispensing via boost compressor.
- The pipeline gas case is valid only for locations with existing infrastructure.

Assumptions for emissions and fuel economy calculations:

- Where available, actual vehicle data are used.
- Modeled vehicles are based on 900 kg PNGV Glider for DTI [2] and 650 kg Renault Twingo for PSI studies [3]

- Station sized to serve 100 cars per day with 300-mile range per fill-up. Thus, the on-site storage capacity is a function of the assumed fuel economy of the vehicles.
- Fuel delivery trucks spend 3 hours per delivery (once per week) in the local, urban area, traveling an average of 20 mph. Except for battery hybrid vehicle stations, which are serviced once every two weeks.
- Fuel delivery trucks are assumed to be powered by a heavy-duty diesel and have a fuel economy of 6.7 miles per gallon, based on Ref. [6].
- On-site POX generator produces emissions are similar to the SMR, multiplied by 1.73, per Ref. [7].

Table 1 presents fuel economy values for alternative vehicles from a variety of sources. Figure 3 shows the results.

Table 1. Fuel economy estimates, miles per gallon-gasoline equivalent, for alternative vehicles

| Study / case | Reference | Driving cycle | DirectH2 Fuel Cell | H2 ICE | Methanol FCV | Gasoline FCV | Battery hybrid | Advanced ICE |
|-------------------------------------|-----------|--------------------------|--------------------|--------|--------------|--------------|----------------|--------------|
| Based on DTI Studies | 1,2 | Accelerated combined EPA | 82 | | 49 | 42 | | 40 |
| Based on PSI Studies | 3 | NEDC | 122 | 54.7 | 46.3 | 85.7 | | 52 |
| Based on Ogden Studies | 4 | Combined FHDS/ FUDS | 102 | | 67 | 62 | | |
| Based on Methanol Institute Studies | 8 | Unknown | 85 | | 65 | 60 | 65 | |
| Measured Value | 9,10 | Road experience | | 26.5 | | | 65 | |
| Ford data or projections | 11 | US FTP (?) | 66 | 47 | | | | 34 |
| Based on Matador studies | 12 | US FTP, NEDC | | | | | 59 | |

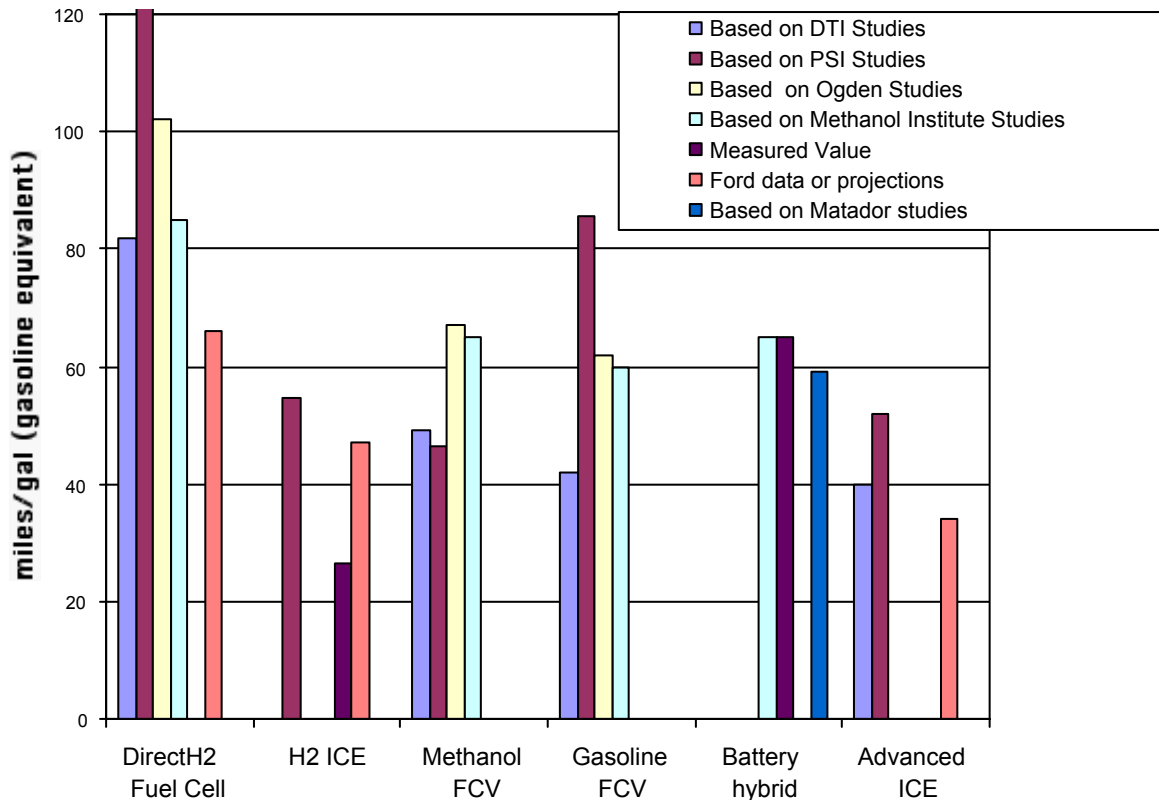


Figure 3: Fuel economy comparison for alternative vehicles

The impact on fuel economy of storing hydrogen as a cryogenic liquid or in a metal hydride, rather than as a compressed gas was estimated using the approach that a 1 kg change in the storage system weight corresponds to a 1.5 kg change in vehicle weight. The results, which are based on the original base case of 75 mpg, are presented in Table 2.

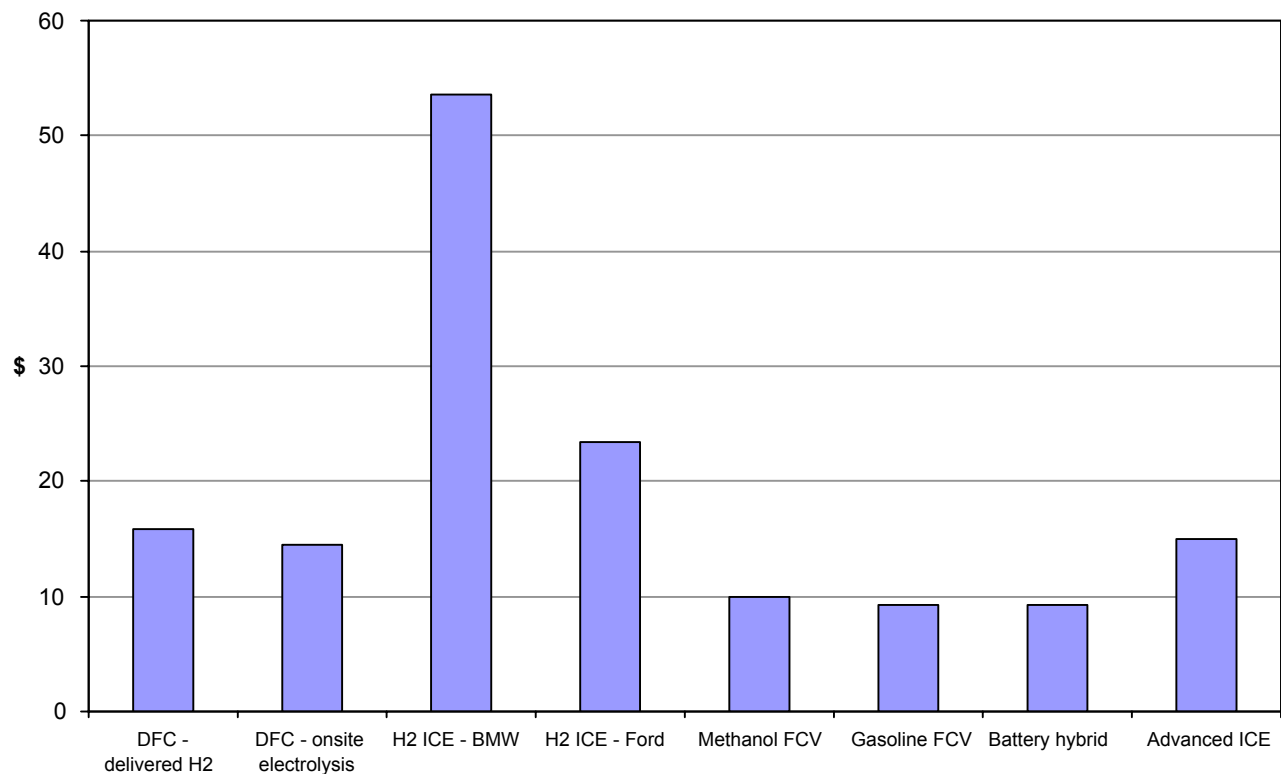
Table 2: Comparison of hydrogen fuel cell vehicles with alternative storage types, based on 75 mpg for compressed gas storage

| Vehicle / storage type | Reference or source | mpg |
|----------------------------|---------------------|------|
| DFC-Compressed gas storage | Original base case | 75 |
| DFC-Liquid storage | 13,14 | 76.5 |
| DFC-MH storage | 13,14 | 66 |

Table 3 presents the cost assumptions (per kg or gal of fuel) for the various fuels, along with the fuel economy value used to estimate the cost of a 300-mile fill-up. Hydrogen costs were taken from the first interim report on this study, assuming full utilization of the station. Figure 4 shows the results.

Table 3: Projected cost for 300-mile fill-up of alternative vehicles and fuels

| | fuel economy (miles/gal - gasoline equivalent) | Reference or source for fuel economy value | fuel mass per 300 mile fill-up, kg | fuel mass per 300 mile fill-up, gal | fuel cost, \$/kg (\$/gal) | Reference or source for fuel cost | \$/300 mile fill-up |
|---------------------------|--|--|------------------------------------|-------------------------------------|---------------------------|-----------------------------------|---------------------|
| DFC – delivered H2 | 89 | average | 3.4 | | 4.7 | This study | 15.8 |
| DFC – onsite electrolysis | 89 | average | 3.4 | | 4.3 | This study | 14.5 |
| H2 ICE – BMW | 26.5 | 9 | 11.4 | | 4.7 | This study | 53.58 |
| H2 ICE – Ford | 47 | 11 | 5 | | 4.7 | This study | 23.5 |
| Methanol FCV | 55 | average | 35.9 | | 0.275 | 4, 5, 16 | 9.88 |
| Gasoline FCV | 60 | 8 | | 4.62 | 2 | Pump price | 9.24 |
| Battery hybrid | 60 | average | | 4.62 | 2 | Pump price | 9.24 |
| Advanced ICE | 40 | average | | 7.5 | 2 | Pump price | 15 |

**Figure 4:** Cost of 300-mile Fill-up for Alternative Vehicles

Tailpipe emissions for alternative vehicles are listed below (CO in Table 4, NO_x in Table 5, HC+VOC in Table 6, and GHG in Table 7). The combined results are shown in Figure 5.

Table 4: Tailpipe CO emissions for alternative vehicles, g/mi

| | Reference | Direct Fuel Cell Vehicle | H2 ICE | Methanol FCV | Gasoline FCV | Battery Hybrid | Advanced ICE |
|--------------------------|-----------|--------------------------|--------|--------------|--------------|----------------|--------------|
| Based on DTI studies | 1,2 | 0 | | 0.0035 | | 3.514 | 5.71 |
| Based on PSI studies | 3 | 0 | | 0.00134 | 0.013 | | 1.280 |
| Based on Methanex report | 17 | 0 | | 0.0016 | | | |
| Based on Ford data | 11 | 0 | 0.0003 | | | | 10.4 |
| Based on Matador report | 12 | | | | | 0.1 | |

Table 5: Tailpipe NO_x emissions for alternative vehicles, g/mi

| | Reference | Direct Fuel Cell Vehicle | H2 ICE | Methanol FCV | Gasoline FCV | Battery Hybrid | Advanced ICE |
|--------------------------|-----------|--------------------------|--------|--------------|--------------|----------------|--------------|
| Based on DTI studies | 1,2 | 0 | | | | 0.338 | 0.55 |
| Based on PSI studies | 3 | 0 | 0.0256 | .00027 | .003 | | 0.102 |
| Based on Methanex report | 17 | 0 | | .0025 | | | |
| Based on Ford data | 11 | 0 | 0.02 | | | | 1.43 |
| Based on Matador report | 12 | | | | | 0.123 | |

Table 6: Tailpipe HC + vehicle VOC emissions for alternative vehicles, g/mi

| | Reference | Direct Fuel Cell Vehicle | H2 ICE | Methanol FCV | Gasoline FCV | Battery Hybrid | Advanced ICE |
|--------------------------|-----------|--------------------------|--------|--------------|--------------|----------------|--------------|
| Based on DTI studies | 1,2 | 0 | | .197 | 0.26 | 0.351 | 0.57 |
| Based on PSI studies | 3 | 0 | | .0134 | 0.025 | | 0.192 |
| Based on Methanex report | 17 | 0 | .0004 | .0034 | | | |
| Based on Ford data | 11 | 0 | | | | | 2.03 |

Table 7: Tailpipe greenhouse gas emissions for alternative vehicles, g CO₂ equivalent/mi

| | Reference | Direct Fuel Cell Vehicle | H2 ICE | Methanol FCV | Gasoline FCV | Battery Hybrid | Advanced ICE |
|--------------------------|-----------|--------------------------|--------|--------------|--------------|----------------|--------------|
| Based on DTI studies | 1,2 | 0 | | 300 | 216 | 200 | 325 |
| Based on PSI studies | 3 | 0 | | 112 | 128 | | 172 |
| Based on Methanex report | 7 | 0 | | 176.2 | | | 234 |
| Based on Ford data | 11 | 0 | 1.4 | | | | 314 |

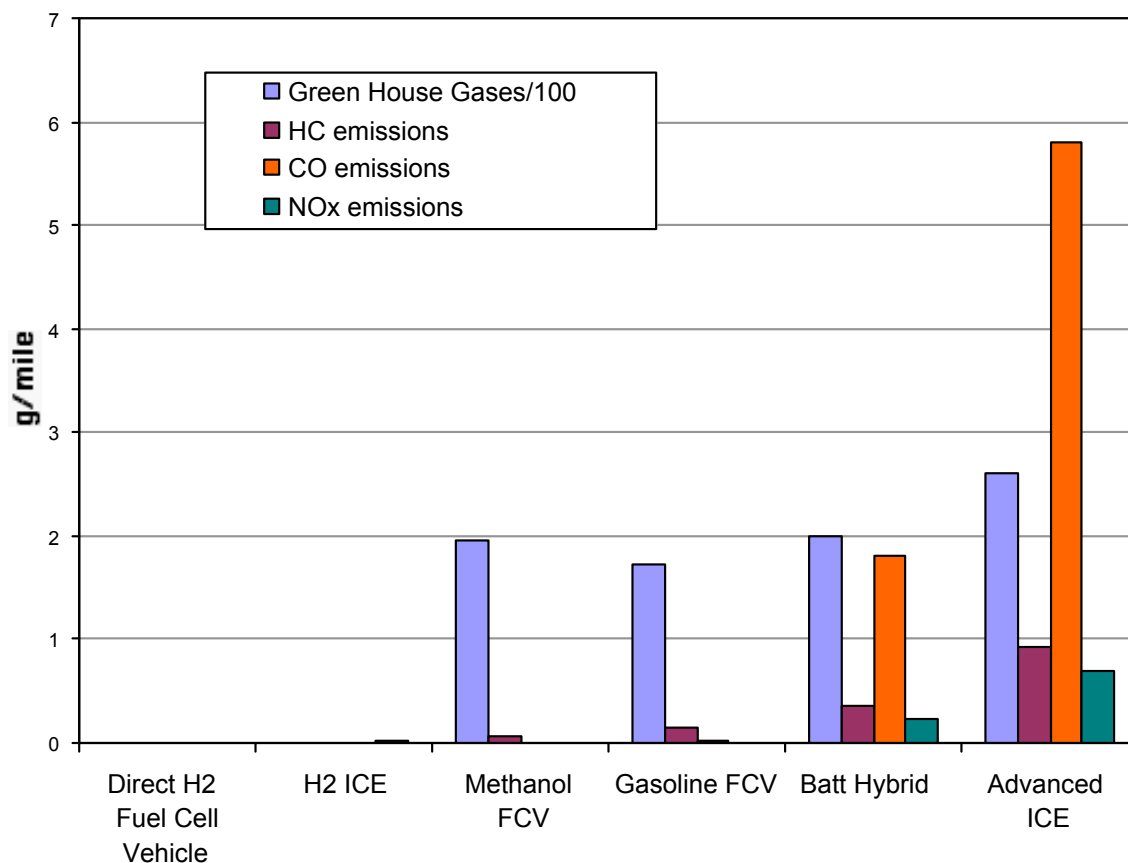


Figure 5: Tailpipe Emissions for Alternative Vehicles

Emissions from station operations or delivery of fuel to the station have been estimated for the various station configurations. These are primarily engine pollutants and fuel volatiles for the cases with fuel delivery, and green house gases for the cases with on-site hydrogen production from natural gas. The two cases with virtually no local emissions are the pipeline delivery of hydrogen and production by electrolysis. For these two cases the major emissions occur elsewhere - at the central reformer and/or electric power station. Only renewable production of hydrogen avoids real-time air emissions throughout the system.

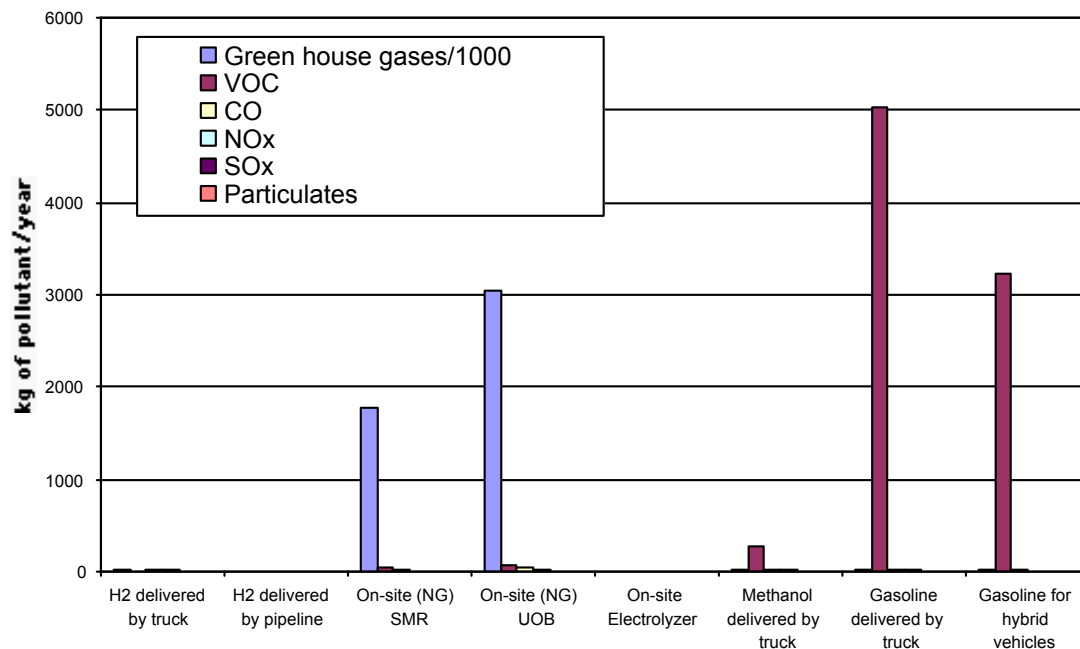
The estimated local emissions from truck delivery are presented in Table 8. Emissions from steam methane reforming of natural gas were taken from a number of sources. As shown in Table 9, the estimates vary from study to study, depending on assumptions and size of the reformer. The DTI study most closely resembles the parameters of this study and so these values were used. Local emission results are shown in Figures 6 and 7.

Table 8: Local (station) emissions due to truck delivery of liquid fuel, kg/yr

| | H2 delivered weekly by truck, truck tailpipe emissions | Reference or source | Methanol delivered by truck, additional fuel emissions | Methanol or gasoline delivered by truck, truck tailpipe emissions | Gasoline delivered by truck, additional fuel emissions | Reference s for volatile fuel emissions | Gasoline for hybrid vehicles, delivered every two weeks |
|--------------|--|---------------------|--|---|--|---|---|
| GHG/1000 | 23.334 | 18 | | 23.334 | | | 11.667 |
| VOC / HC | 6.55 | 19 | 272 | 6.55 | 5032 | 21,1 | 3234.28 |
| CO | 31.2 | 19 | | 31.2 | | | 15.6 |
| NOx | 12.5 | 19 | | 12.5 | | | 6.25 |
| SOx | 7.3 | 20 | | 7.3 | | | 3.65 |
| Particulates | 0.4 | 17 | | 0.4 | | | 0.2 |

Table 9: Local (station) emissions from on-site steam methane reformer, kg/yr

| Source | Spath | DTI | PSI | Methanex |
|--------------|--------|--------|--------|----------|
| Reference | 22 | 1 | 3 | 7,17 |
| GHG/1000 | 1298.7 | 1852.1 | 1401.6 | 2515.2 |
| VOC | | 38 | | |
| CO | 11.7 | 28 | | |
| NOx | 131 | 9.5 | | |
| Particulates | | | | 3.2 |

**Figure 6:** Emissions from Alternative Refueling Station Configurations

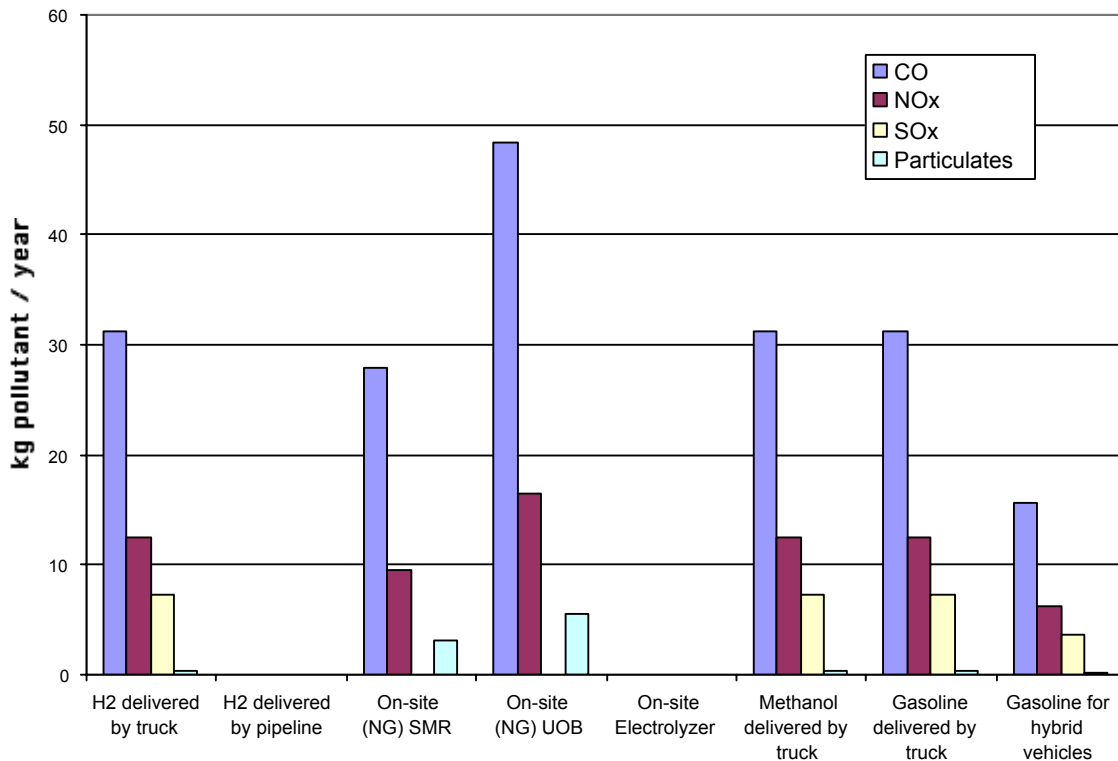


Figure 7: Air Pollutants from Alternative Refueling Stations

From the transportation analysis done to date, the major conclusions are:

- The direct hydrogen fuel cell vehicle has the best fuel economy of all the alternatives considered.
- As a result, the cost of a 300-mile fill-up is comparable with other low-cost alternatives: methanol and battery hybrid vehicles.
- The lowest cost hydrogen comes from pipeline hydrogen (where infrastructure exists) or electrolysis.
- Tailpipe emissions for hydrogen vehicles are zero or negligible, making hydrogen vehicles the best choice for urban driving. Station emissions for hydrogen stations are lowest for pipeline hydrogen and on-site production by electrolysis.

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TASK 14 – PHOTOELECTROLYTIC PRODUCTION OF HYDROGEN

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Introduction

Task 14 focuses on the development of water photoelectrolysis. Simplified, this can be described as a process whereby sunlight is used to split water into hydrogen and oxygen upon illumination of an electrochemical device that applies photoactive electrode material. As an alternative, the production of hydrogen can also be achieved by using organic matter as the electron donor instead of water. Overall, the integrated combination of photovoltaics and electrolysis through the application of semiconductor-based photoelectrodes offers great potential for cost reduction compared to the use of two conventional but separate processes.

Task Description

The overall objective of Task 14 is to significantly advance the fundamental and applied science in the area of photoelectrolysis of water over a period of three to five years. More specifically, it is aimed to evaluate performance data regarding practical system efficiency and device lifetime. From a scientific point of view, key investigations are focusing on semiconductor materials and structures, photosensitive dyes, integrated photovoltaics/electrolysis systems, and novel single- and dual-bed reactor arrangements. The participants are undertaking research within the framework of two coordinated subtasks.

Subtask A: Material Studies

Subtask A concerns (a) the improvement of light absorption of wide-bandgap semiconductor materials by dye-sensitization and other techniques and (b) the development of catalytic and protective layers for photoelectrochemical (PEC) cells.

It is aimed that demonstration systems using dye-sensitized tandem cell devices can achieve reliable water cleavage with a sunlight-to-hydrogen conversion efficiency of beyond 5%.

Subtask B: System Studies

Subtask B concerns (a) the maximization of efficiency of multi-junction water splitting systems and (b) the assessment of reactor system designs for the photoproduction of hydrogen.

Multi-junction systems are being developed and studied with the ultimate aim of reaching a stabilized sunlight-to-hydrogen conversion efficiency of 10%.

Duration

Task 14 started on 1 July 1999 and is scheduled for an initial three-year period, with an option for a two-year extension toward 30 June 2004.

Participation

Japan, Sweden, Switzerland and the United States have been participants since the start of the Task.

Activities & Progress during 2001

The 3rd Task 14 expert meeting was held at the Angström Solar Center in Uppsala, Sweden, 10-12 September 2001. The meeting was well attended, including visitors from non-member countries. Hydrogen experts also gathered during the 1st International Conference on the Hydrogen Age of Asia, Tokyo, 27-28 November 2001).

The following research groups were active in Task 14 during 2001: The National Renewable Energy Laboratories (NREL), the Florida Solar Energy Centre (FSEC), the Hawaii Natural Energy Institute (HNEI) and the University of California (UCal), United States; the University of Uppsala (UniU), Sweden; the University of Geneva (UniG), the University of Bern (UniB) and the Swiss Federal University of Technology (EPFL), Switzerland; and the National Institute of Advanced Industrial Science & Technology (AIST), Japan.

Collaboration via joint investigations, publications, and exchange of researchers, ideas and materials intensified during 2001. Efforts are in progress to link new research teams into the current Program of Work. Particular interest to collaborate has been expressed by researchers from potential new member countries, including Australia, China, Germany, Israel and Mexico. Research on photoelectrochemical (PEC) cells is growing worldwide.

Subtask A: Material Studies

The anodic oxidization of water to oxygen is generally the performance-limiting step in a PEC device. Progress toward performance improvement has primarily been achieved in the areas of light harvesting and corrosion resistance.

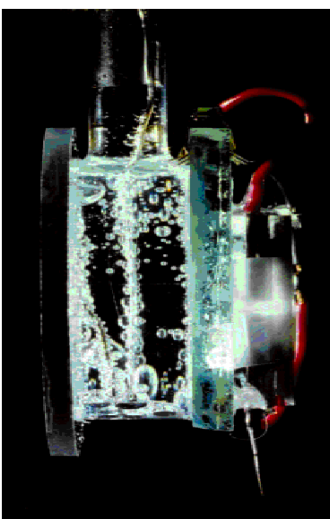


Figure 1: A tandem PEC system for visible light induced water cleavage based on mesoscopic semiconductor films (Source: Graetzel, Swiss Federal University of Technology, EPFL, Switzerland).

Regarding photoanodes, work has been focusing on the development of thin films using nanocrystalline titania (TiO_2), nanostructured polycrystalline tungsten trioxide (WO_3), iron oxide (above all hematite Fe_2O_3), and, as a new stream of effort, a range of promising mixed-oxides (iron, titanium, cerium and molybdenum) and nitrides (indium and tin). Preliminary work has started on applying combinatorial chemistry to better screen and characterize for material choice and doping.

Tungsten trioxide (WO_3) - With a band-gap of about 2.6 eV and a demonstrated resistance to photocorrosion in aqueous solutions, WO_3 thin-films are well matured for photoanode applications in water splitting systems.

At the University of Geneva (UniG), a new production process for multi-layer WO_3 thin films, with an overall thickness of typically about 3 nanometers, has been matured and patented [Santato et al., 2001]. The WO_3 thin films are highly transparent (60-80%; light absorption noticeably limited to the blue portion of the sunlight at below ~ 475 nm) and consist of a network of preferentially oriented nanocrystals. This semiconductor has demonstrated the ability to operate as both an efficient (photocurrents of up to 6 mA/cm^2) and stable solar-driven photoanode for the oxidation of water (so far with an efficiency of about 2.7%) and various organic compounds (e.g. methanol with close to 5% efficiency). The sufficient resistance against photocorrosion in aqueous solutions has been confirmed over a large range of pH, including strongly acidic solutions.

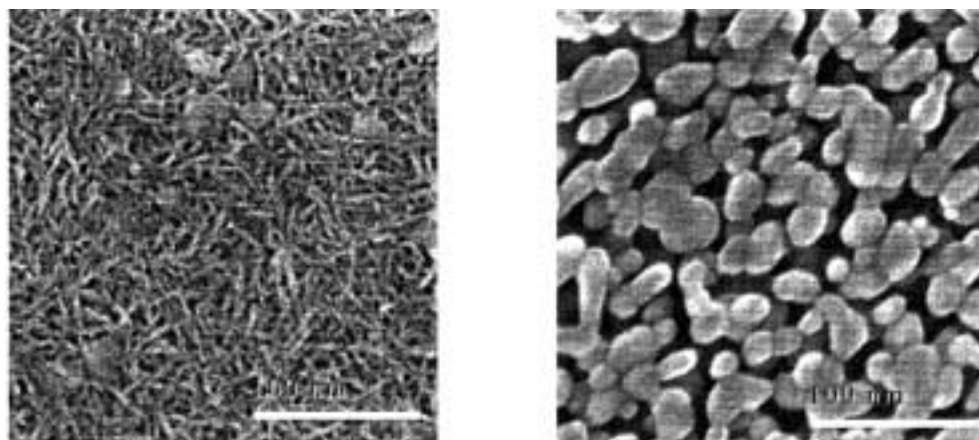


Figure 2: WO_3 films prepared by the deposition of a tungstic acid / PEG colloidal solution and 30-min annealing at 400°C and 500°C respectively (Source: Santato, University of Geneva, Switzerland).

Recently, preliminary research at the University of California (UCal) suggests that doping with, for instance, nickel, copper, iron or cobalt shows promise for further performance increase. Nevertheless, resource limitations and costs in particular continue to encourage the search for alternative photoanode materials, most interestingly hematite.

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) - Iron oxide is seen as a most promising, low-cost, stable candidate for photoanodes in PEC devices, with prime research conducted mainly at the Swiss Federal University of Technology (EPFL), the University of Geneva (UniG) and the University of Augsburg (UniA). Spray pyrolysis, reactive sputtering and liquid phase chemical vapor

deposition (LPCVD) are among the main preparation methods studied for the production of thin-films. The band gap of Fe_2O_3 is expected to be significantly lower than that of WO_3 . Ideally, it should approach the value of 1.8 eV for a dye-sensitized tandem PEC cell for water splitting.

Early in 2001, researchers at the Swiss Federal University of Technology (EPFL) managed to produce stable photocatalytic Fe_2O_3 multi-layers deposited on conducting glass using a spray pyrolysis method. The Ti-doped Fe_2O_3 films produce a photocurrent of over 2 mA/cm^2 under simulated AM-1.5 sunlight using water as the electron source. Once coupled to an appropriate tandem PEC solar cell system, this result corresponds to a solar-to-chemical conversion efficiency of about 3%.

Later in the year, encouraging results were reported by UniG whereby photocurrents of 5-6 mA/cm^2 have been achieved for doped (titanium and aluminum) thin-films ($\sim 3 \mu\text{m}$) tested under simulated AM-1.5 sunlight. When coupled to a tandem PEC cell, this result would correspond to a solar-to-chemical conversion efficiency on the order of 7-8%. The key challenge encountered by all research groups was homogeneity and reproducibility in the particle size of the films. The use of pyrolysis temperatures between 400 and 450°C was found to produce the above-mentioned results.

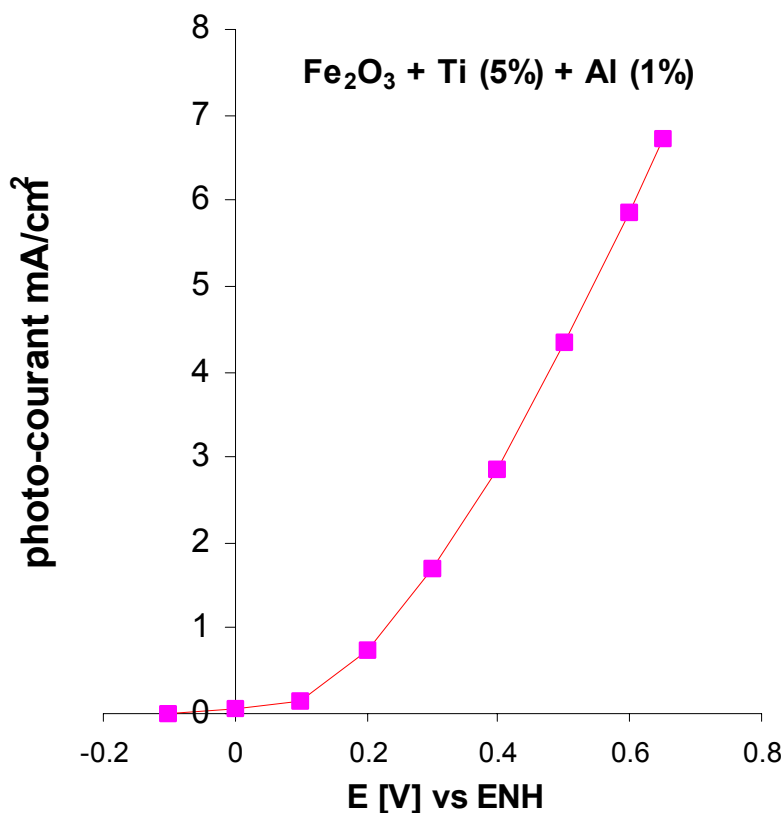


Figure 3: Photocurrents measured for $\alpha\text{-Fe}_2\text{O}_3$ electrodes doped with 5%-Ti and 1%-Al (Source: Augustynski, University of Geneva, Switzerland).

Improvements in the morphology and selective doping of the Fe_2O_3 thin-films are needed to achieve higher photocurrents. Researchers at the National Institute of Advanced Industrial Science & Technology (AIST; Japan) and the Academy of Material Science (UNAM; Mexico) are studying the effects using various semiconductor thin-films. This will provide insight into fine-tuning the conduction and valence bands of the semiconductor materials of interest to PEC devices.

Nitride, carbide & mixed-oxide semiconductor catalysts - Preliminary studies on a variety of nitride, carbide and mixed-oxides have shown interesting potential for stable, alternative photocatalyst materials.

Indium (In) and tin (Sn) nitrides are being studied as possible new electrodes at the University of Uppsala (UniU). InN has an indirect band gap of 1.4 eV and, if made p-type with, for instance, zinc (Zn), could become an interesting alternative photoanode due to its promise of achieving a material with a comparably small overpotential for water splitting.

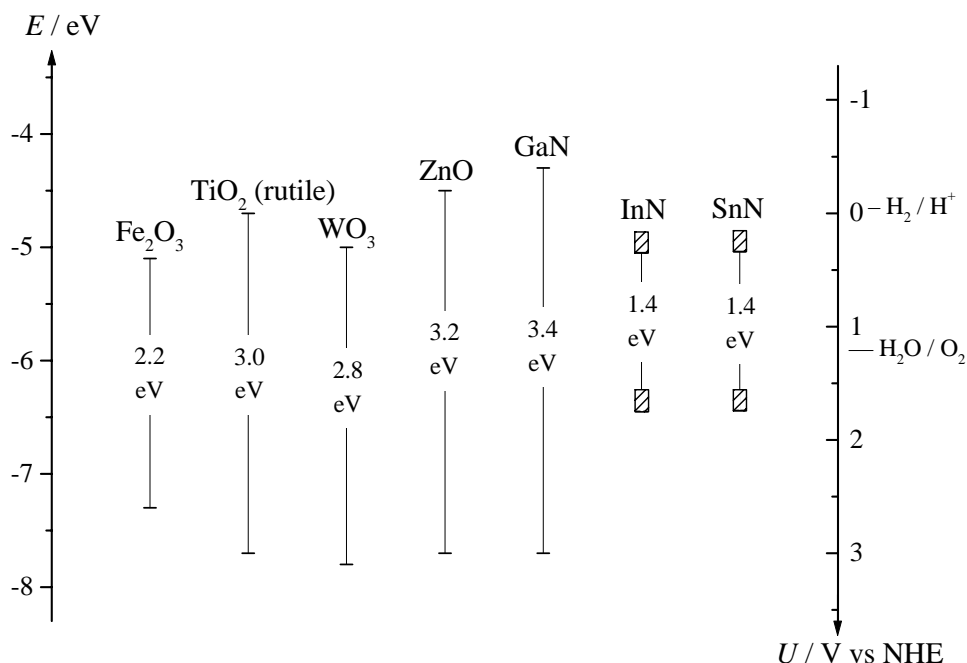


Figure 4: Position of energy bands of common semiconductors and of nitrides at pH 1 with respect to the electrochemical scale. The standard electrode potentials of hydrogen and oxygen are shown for reference (Source: Lindgren, University of Uppsala, Sweden).

Mixed-oxide anode catalysts based on IrO_2 and RuO_2 are being developed at the Norwegian University of Science & Technology (NTNU). As part of a PEM fuel cell at 80°C , polarization values as low as 1.59 V at 1 A/cm^2 have been obtained.

At the Photoreaction Control Research Center (PCRC) of the Japanese National Institute of Advanced Industrial Science and Technology (AIST), a single-particle photocatalyst has been developed that achieves both fast-response hydrogen evolution and oxygen evolution. When

promoted with nickel oxides, mixed-oxide semiconductor powders based on indium (In), niobium (Nb) and/or tantalum (Ta) oxides were found to be stable photocatalysts and have attractive band gaps typically of 2.5 – 2.6 eV. PCRC aims to develop processes that result in nanostructured powders with large specific surface areas (today $\sim 1 \text{ m}^2/\text{g}$) for water splitting applications in aqueous suspension under visible light irradiation.

Zeolites - Zeolites can be combined with a semiconductor photocathode to act as antenna system for light harvesting, as well as transport in the oxygen evolution part of a water-splitting PEC cell [Calzaferri et al., 2001]. At the University of Bern (UniB), a two-compartment PEC has been operated using a nanostructured silver chloride zeolite layer as the photocatalytic anode in combination with platinized silicon as the counter electrode. Maximum hydrogen evolution was observed in the pH range of between 4 and 6. Photoactivity of AgCl extends from the UV into the visible light region in a process known as self-sensitization.

Light-harvesting pigments & dyes - Pigments and dyes can act as photo-catalytic agents in solar water-splitting PEC devices and schemes.

At the Florida Solar Energy Centre (FSEC), various new organic pigments have been studied, whereby semi-empirical molecular orbital calculations based on voltammetry and PM3 were confirmed to accurately predict the oxidative water-splitting ability of pigment candidates [Slattery et al., 2001]. The best performing pigments (e.g. perylene) have then been made into films containing 1.0%-wt of Pt catalyst for illumination with Xenon lamps.

Using a three-dye antenna on a zeolite-L structure, light harvesting over the whole visible spectrum with subsequent energy transport leading to fluorescence at the cylindrical zeolite-L ends has, for the first time, been demonstrated at the UniB. Attempts are being made to use this system for the development of a novel thin-layer solar cell in which light absorption and the creation of an electron-hole pair are spatially separated.

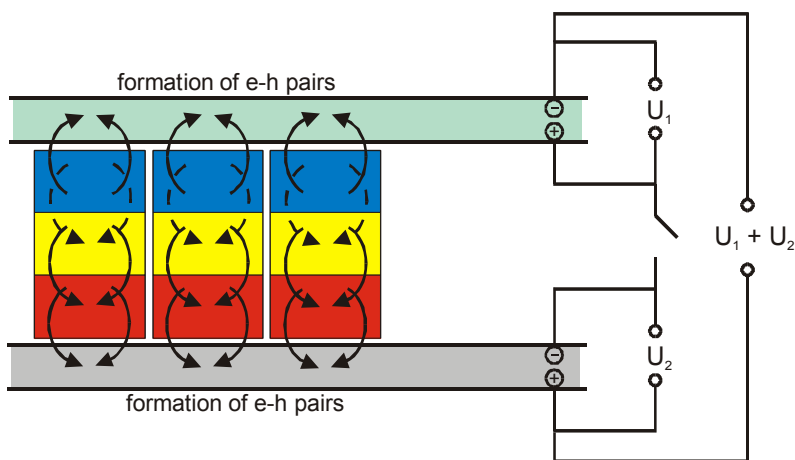


Figure 5: Tandem solar cell, where mono-directional antenna systems with blue, yellow and red dyes are put between two n-type semiconductors with different band gaps (Source: Calzaferri, University of Bern, Switzerland).

The new series of “black” panchromatic ruthenium(II) sensitizers (ruthenium-II polypyridyl complexes) developed at the EPFL achieve improved performance when anchored to nanocrystalline TiO_2 films for PEC or PV application. Sensitization extends over the whole visible range and into the near-IR region up to 940 nm, yielding over 80% incident photon-to-current efficiencies (IPCE) in the plateau between 500 nm and 750 nm. A short circuit photo current density (isc) of around 18 mA/cm^2 was achieved for a $12 \mu\text{m}$ thick TiO_2 electrode under AM 1.5. Excellent stability toward water-induced desorption has also been confirmed. The spectral onset of this novel ruthenium “black” dye, when used in the dye-sensitized solar cell, corresponds perfectly to the optimal value of 1.4 eV.

Subtask B: System Studies

Monolithic devices that combine single-gap or multi-junction photovoltaic (PV) cells with electrolysis systems and two-stage, as well as dual-bed reactor systems that incorporate oxygen- and hydrogen-evolving photocatalyst suspensions are being studied at various research institutes around the world.

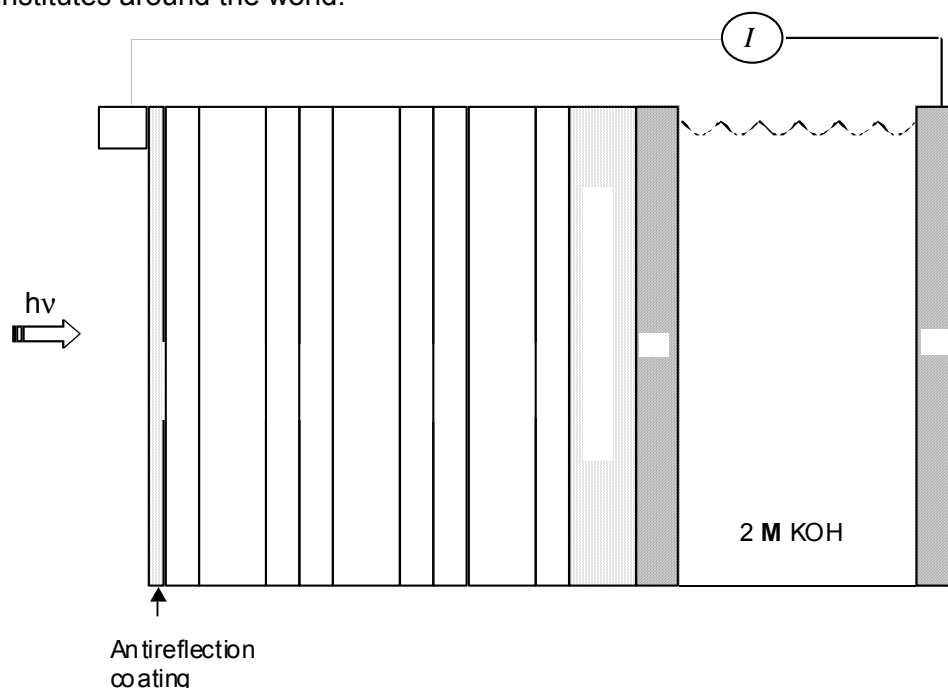


Figure 6: Integrated, monolithic, multi-junction (triple-junction α -Si on stainless substrate) photovoltaic / electrolysis system for photocatalytic water splitting (Source: Turner, National Renewable Energy Laboratories, USA).

Multi-junction systems - The development of integrated multi-junction photoelectrodes, comprising semiconductor, catalytic and protective thin films deposited on low-cost substrates, are getting increased R&D attention at the National Renewable Energy Laboratories (NREL), the Hawaii Natural Energy Institute (HNEI) and the Academy of Material Science, Mexico (UNAM). Much of the work has been based on photoreactor structures based on multi-junction α -Si and CIGS solar cells.

Amorphous silicon carbide (α -SiC) is being studied at NREL [Sebastian et al, 2001] as a protective layer for triple-junction solid-state/PEC water splitting systems. Such systems are also being investigated at HNEI. There, NiMo films for hydrogen-evolution and FeNiO_x films for oxygen-evolution are being used. In addition, researchers at UNAM are studying the effects of doping porous silicon thin-films and the use of copper-indium-gallium-diselenide (CIGS) as alternatives to α -Si for solid-state/PEC water splitting systems.

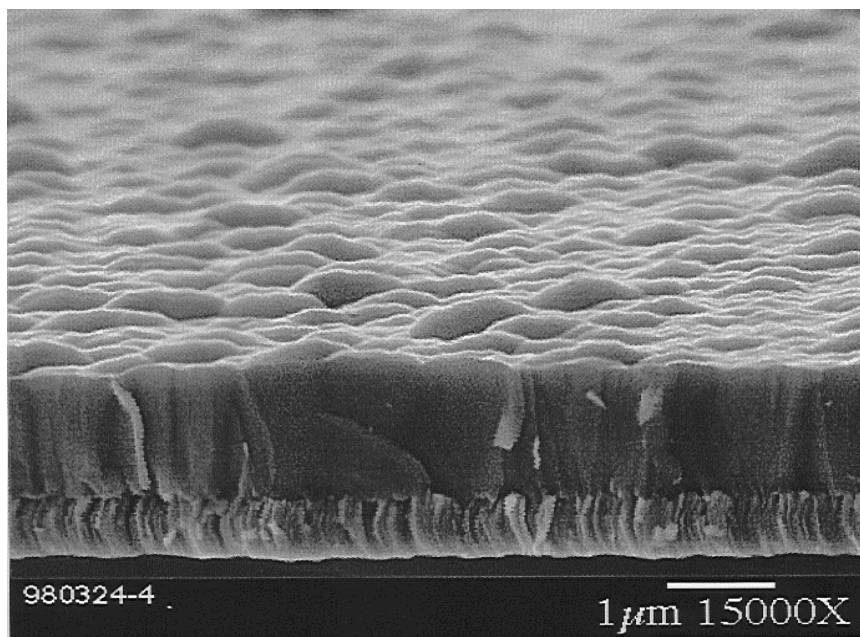


Figure 7: Cross-sectional SEM photograph for a representative CIGS thin film electro-deposited for 50 minutes and annealed in Se atmosphere at 500°C (Source: Joseph, Academy of Material Science, Mexico).

Using a new, stable, reverse-design triple-junction α -Si laboratory cell, a solar-to-hydrogen conversion efficiency of 4% was measured at NREL. Device stability was accomplished by surface protection using α -SiC on the illuminated side and ZnO at the backside. At HNEI, “hybrid” PEC devices are being investigated in which solid-state junctions are placed behind a current-matched electrochemical photojunction to generate the bias for water splitting.

Dual-bed system - At the Florida Solar Energy Centre (FSEC), an electrochemical equivalent of a dual-bed PEC system has demonstrated that a 0.1-M redox mediator (ferro-/ferricyanide) couple can support photocurrents of up to 10 mA/cm². Indanthrone on p-type NiO was used as the photocatalyst. Furthermore, Iridium (Ir) deposited as a co-catalyst on TiO₂ was newly established as, thus far, the best performing inorganic oxidative water-splitting photocatalyst for the dual-bed PEC reactor concept.

Two-step system using powder catalyst suspension - At the Photoreaction Control Research Center (PCRC) of the Japanese AIST, preliminary laboratory efforts have shown great promise for the design of a two-step water splitting system composed of two different TiO₂

(anatase and rutile) and a iodine-based (I^-/IO_3^-) shuttle redox mediator. This mimics the Z-scheme mechanism in photosynthesis. Furthermore, hydrogen-evolution from water under visible light ($> 420 \text{ nm}$) has been achieved with new dye-sensitized oxide semiconductor power catalysts (e.g. Eosin-Y fixed to TiO_2) using a silane-coupling reagent.

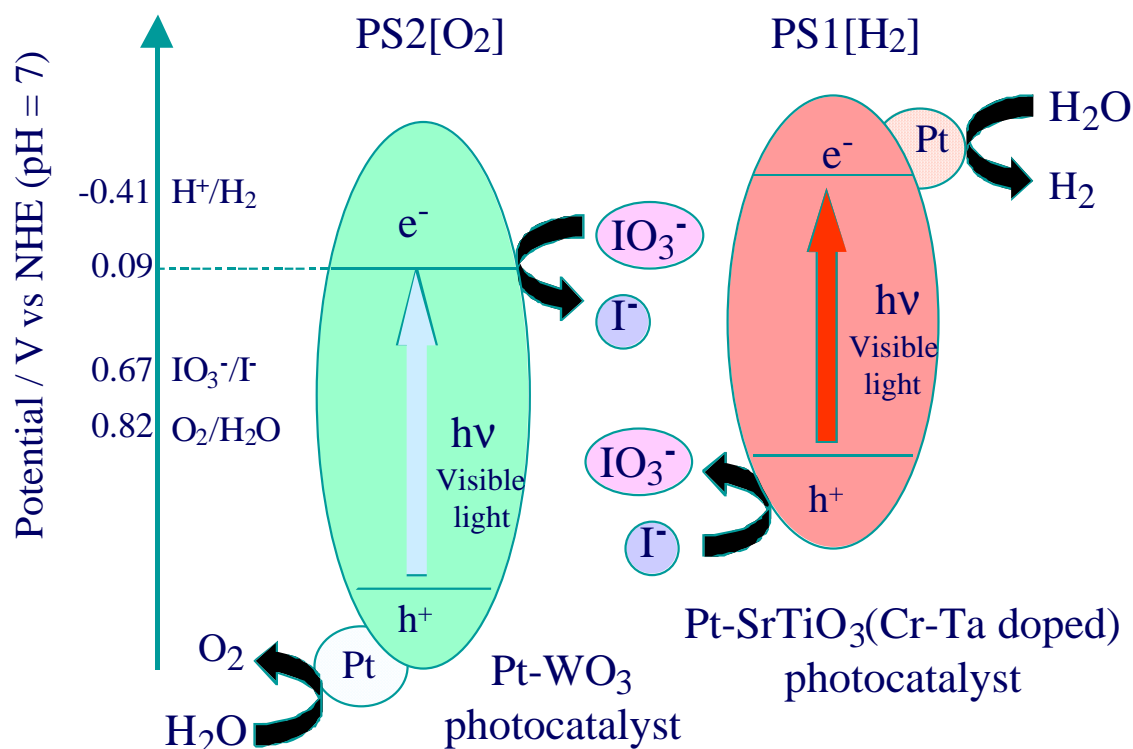


Figure 8: Reaction mechanism for two-step photocatalytic water splitting system using powder catalyst in suspension. The system mimics the Z-scheme in natural photosynthesis (Source: Arakawa, Photoreaction Control Research Centre, AIST, Japan).

Future Activities

Research in 2001 has indicated significant research opportunities regarding the performance improvement of PECs in the areas of semiconductor materials, light-harvesting dyes and photocatalyst stability. The goals of achieving a stable, net sunlight-to-hydrogen conversion efficiency of 5% for dye-sensitized tandem cell devices and 10% for monolithic multi-junction systems seem within reach.

Task 14 is aiming to develop a two-year extension program (1 July 2002 – 30 June 2004) with the key objectives being to: (a) advance science; (b) study engineering solutions; (c) build a new demonstration system; (d) expand collaboration; and (e) promote photoelectrolysis.

Three major opportunities have been identified to demonstrate an advanced PEC system as part of the extension program using either existing large laboratory or commercial manufacturing equipment. They comprise: (a) CIGS / Fe_2O_3 ; (b) $\infty\text{-Si}$ / IrRuO_x ; and (c) an advanced version of TiO_2 -dye-cell / WO_3 . System choice will be made toward the end of the first year of the extension program.



Figure 9: Production-line TiO_2 dye-cell solar panel (40 Watt per m^2). The panel contains 24 series-connected tiles, encapsulated in a transparent insulating polymer and laminated between two glass panes (Source: Sustainable Technologies International, Australia).

Recommended Reading

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TASK 15 - PHOTOBIOLOGICAL HYDROGEN PRODUCTION

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Introduction

Biological hydrogen production, the production of hydrogen by microorganisms, has been an active field of basic and applied research for over two decades, with significant applied R&D programs supported in Europe, Japan and the United States. Realization of practical processes for photobiological hydrogen production from water using solar energy would result in a major, novel biological source of sustainable and renewable energy, without greenhouse gas emissions or environmental pollution. However, development of such practical processes will require significant scientific and technological advances, and relatively long-term (>10 yr) basic and applied R&D.

Photobiological hydrogen production was a component of the prior Task 10 of the IEA Hydrogen Agreement, and has evolved into the independent Task 15. This effort covers research areas and needs at the interface of basic and applied R&D that are of mutual interest to the countries and researchers participating in the IEA Hydrogen Agreement. Task 15 provides for the establishment of collaborative research projects among participating countries in a coordinated program.

Task Description

Task 15 deals specifically with "biophotolysis", i.e. the biological production of hydrogen from water and sunlight using microalgal photosynthesis. The overall objective of Task 15 is to advance the basic and early-stage applied science in this area. This will allow an evaluation of the potential of such a technology to become a renewable energy source for the 21st Century. The biophotolysis process uses microalgae, either green algae or cyanobacteria, to fix CO₂ into carbohydrates, which are used by the algae to generate H₂ gas, first in the dark by fermentations and then in the light through photosynthesis-coupled reactions. The tentative Task 15 goal is to achieve a light conversion of 3% into hydrogen gas.

The main objective of Task 15 is to develop hydrogen production by microalgae (both green algae and cyanobacteria) emphasizing on early-stage applied research on biophotolysis processes with intermediate CO₂ fixation. This research will help to provide the advances required to achieve the practical efficiencies and cost goals of biological hydrogen production. The Task investigates microalgal hydrogen metabolism, both in the dark and in the light, as well as the mechanisms that would allow the photosynthetic processes and hydrogen evolution reactions to achieve their maximum possible efficiencies. In addition, subsidiary metabolic processes require investigation, such as the efficient accumulation of large amounts of carbohydrates, the regulation of the photosynthetic processes and the recycling of the algal cells after hydrogen evolution is completed. Complex underlying genetic mechanisms and biochemical pathways are involved in these physiological processes and require significant research efforts.

The work in Task 15 is divided into four Subtasks; (A) Light-driven Hydrogen Production by Microalgae; (B) Maximizing Photosynthetic Efficiencies; (C) Hydrogen Fermentations; and (D): Improve Photobioreactor Systems for Hydrogen Production.

Duration

Task 15 was began work on 1 July 1999 and is scheduled for a three-year period, with an option for a two-year extension.

Participation

Present participants in Task 15 are Canada, Japan, Norway, the Netherlands, Sweden and the United States.

Activities and Progress During 2001

(1) Two Expert-meetings

a) March 26-27, 2001, in Porto (Portugal) with eight active participants:

Hallenbeck, Patrick; Univ. Montreal, Canada
Janssen Marcel; Wageningen Univ. The Netherlands
Källqvist, Torsten; Kjelsås, Norway
Lindblad, Peter; Uppsala Univ., Sweden
Seibert, Michael; NREL, Golden, USA
Tamagnini, Paula; Porto, Portugal
Van Ooteghem, Suellen; NETL, USA
Wright, Philip; Edinburgh, UK

b) September 7-12, 2001, in Szeged, Hungary. This meeting was organized as a joint workshop, with the title *BioHydrogen*, between the IEA Hydrogen Agreement Task 15 and the European COST Action 8.41 (*Biological and Biochemical Diversity of Hydrogen Metabolism*) with, in total, thirty-one participants:

Axelsson, Rikard; SE (Task 15)
Blokesh, Melanie; D
Böck, August; D
Burja, Adam; UK
Boison, Gudrun; D
Cammack, Richard; UK
Collet, Christophe; CH
Cournac, Laurent; FR
Hallenbeck, Patrick; CA (Task 15)
Hanczar, Timea; HU
Happe, Thomas; D
Janssen, Marcel; NL (Task 15)
Kim, Mi-Sun; Korea
Kovács, Kornél; HU

Källqvist, Torsten; NO (Task 15)
Lindberg, Pia; SE (Task 15)
Lindblad, Peter; SE (Task 15)
Lopez de Lacey, Antonio; ES
Lenz, Oliver; D
Miyake, Jun; JP (Task 15)
Peltier, Gilles; FR
Rákhely, Gábor; HU
Ruiz-Argüeso, Tomas; ES
Schwitzer, Jean-Paul; CH
Schultz, Rudiger; D
Seibert, Michael; USA (Task 15)
Tamagnini, Paula; PT
Tomiyama, Masamitsu; JP (Task 15)
Van Ooteghem, Suellen; USA (Task 15)
Vignais, Paulette; FR
Wright, Philip; UK

(2) General Progress

- a) Task 15 was presented and discussed at the 12th International Congress on Photosynthesis, Brisbane (Australia) 18-23 August 2001

Biohydrogen: International collaboration and Status & potential of using cyanobacteria

Molecular hydrogen (H₂) is an environmentally clean energy-carrier that may be a valuable alternative to the limited fossil fuel resources of today. Biological hydrogen production, the production of H₂ by microorganisms, has been an active field of basic and applied research for many years. Realization of practical processes for photobiological hydrogen production from water using solar energy would result in a major, novel source of sustainable and renewable energy, without greenhouse gas emissions or environmental pollution. In the present communication, I will discuss present activities and achievements within the four subtasks of Annex 15, Photobiological hydrogen production, of the IEA Hydrogen Agreement;

- A. Light-driven Hydrogen Production by Microalgae
- B. Maximizing Photosynthetic Efficiencies
- C. Hydrogen Fermentations
- D. Improve Photobioreactor Systems for Hydrogen Production

In N₂-fixing cyanobacteria, H₂ is mainly produced by nitrogenases, but its partial consumption is quickly catalyzed by a unidirectional uptake hydrogenase. In addition, a bi-directional enzyme may also be present. I will summarize present knowledge focusing on recent advances using molecular techniques, outline strategies for improving the capacity of H₂-production, and discuss recent achievements using genetically modified cyanobacteria in a small scale photobioreactor.

- b) A most wanted book, ***Biohydrogen II***, has been published with contributions from leading international experts and covers the breadth of biohydrogen research and development, from

production to genetic engineering and molecular biology. This volume is designed to be an invaluable resource for researchers and other professionals who wish to obtain an overview of biohydrogen R&D. Contributions from IEA Hydrogen Agreement Task 15 are indicated in **bold** and with an *.

Biohydrogen II - PERGAMON. ISBN: 0-08-043947-0 (284 pages)

Edited by: J. Miyake, National Institute for Advanced Interdisciplinary Research, AIST/MITI, Tsukuba, Ibaraki, Japan; T. Matsunaga, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan; A. San Pietro, Indiana University, Bloomington, Indiana, USA

Hydrogen Production

***Hydrogen production by photosynthetic bacteria: culture media, yield and efficiencies** (J.S. Rocha, M.J. Barbosa, R.H. Wijffels).

Hydrogen and Poly- (hydroxy) alkanolate production from organic acids by photosynthetic bacteria (N. Noparatnaraporn, K. Takeno, K. Sasaki).

***Hydrogen from Biomass** (T. Wakayama, J. Miyake).

Hydrogen photoproduction from starch in algal biomass (A. Ike, H. Kawaguchi, K. Hirata, K. Miyamoto).

Photobiological hydrogen production and nitrogenase activity in some heterocystous cyanobacteria (H. Masukawa, K. Nakamura, M. Mochimaru, H. Sakurai).

***Strategies for improving oxygen tolerance of algal hydrogen production** (M. Seibert, T. Flynn, M.L. Ghirardi).

Hydrogen World

Emerging hydrogen energy systems and biology (T. Ohta).

***Biohydrogen: an opportunity for international cooperation** (A. San Pietro, J.R. Benemann).

Hydrogenotrophy - a new aspect of biohydrogen (Y. Igarashi).

Biochemical and Metabolic Systems

***Maximising photosynthetic efficiencies and hydrogen production in microalga cultures** (J. Polle, S. Kanakagiri, J.R. Benemann, A. Melis).

A scheme for developing the yield of hydrogen by fermentation (S. Tanisho).

Molecular Biology

***Cyanobacterial hydrogenases and biohydrogen: present status and future potential** (P. Lindblad, P. Tamagnini).

***Integration of hydrogen evolving systems with cellular metabolism: the molecular biology and biochemistry of electron transport factors and associated reductases** (P.C. Hallenbeck).

Genetic Engineering

Screening of marine photosynthetic microorganisms and hydrogen production (T. Matsunaga, H. Takeyama).

Metabolic engineering approaches for the improvement of bacterial hydrogen production based on *Escherichia coli* mixed acid fermentation (K. Sode, S. Yamamoto, M. Tomiyama).

***Molecular Handling of Hydrogenase** (M. Miyake, J. Schnackenberg, C. Nakamura, Y. Asada, J. Miyake).

Photobioreactors

Production of hydrogen by an *Anabaena variabilis* mutant in a photobioreactor under aerobic outdoor conditions (A.S. Fedorov, A.A. Tsygankov, K.K. Rao, D.O. Hall).

Hydrogen photoproduction by purple bacteria: immobilized vs. suspension cultures (A.A. Tsygankov).

Photobioreactor design for photobiological production of hydrogen (J.C. Ogbonna, H. Tanaka).

Hydrogen production from food processing wastewater and sewage sludge by anaerobic dark fermentation combined with photo-fermentation (M-S. Kim, T.J. Lee, Y.S. Yoon, I.G. Lee, K.W. Moon).

c) Scientific Exchange

Several putative scientific exchanges were identified during the two Experts Meetings. In addition, many of the participating laboratories are continuously exchanging ideas, suggestions, comments, etc., improving the overall scientific outputs within the respective projects.

A specific exchange occurred July 2001: Röbbbe Wünschiers (Postdoctoral Researcher in Uppsala, Sweden) visited and worked for one week in the laboratory of Michael Seibert at NREL (Golden, CO, US) and also met with Anastasios Melis at UC-Berkeley (CA, USA).

d) New Members

The Netherlands joined Task 15 during 2001. Observers from Hungary, Italy, the United Kingdom and Portugal participated in the Experts Meetings with the aim of becoming members during 2002.

e) BioHydrogen 2002

An international conference held under auspices of IEA Hydrogen Agreement Task 15, *Photobiological Hydrogen Production*, and EU COST 8.41, *Biological and Biochemical Diversity of Hydrogen Metabolism*, is being planned to be held in Ede, the Netherlands, April 21-24, 2002.

Objectives of the Conference: Hydrogen production by microorganisms has been an active field of basic and applied research for many years. Realization of practical processes for biological hydrogen production would result in a major, novel source of sustainable and renewable energy, without greenhouse gas emissions and environmental pollution.

The aims of Biohydrogen 2002 are to summaries the state of the art of biological hydrogen production, evaluate current progress on early-stage applied science in this area of research and development, and to identify promising research directions for the future. Biohydrogen 2002 coincides with the end of the first three years of Task 15.

A secretariat (at Wageningen University), Organizing Committee and Advisory Board have been established. The Proceedings will be published as a special issue of the International Journal of

Hydrogen Energy (IJHE). All participants of Biohydrogen 2002 will receive a hardbound copy of these proceedings.

f) Extension of Task 15

The extension of Task 15 after the initial three years has been discussed. Both the countries that joined Task 15 in the beginning and those joining later or being in a process of signing would like to both continue and to expand this most fruitful cooperation/network.

(3) Progress Related to Subtasks

a) Subtask A: Light-driven Hydrogen Production by Microalgae

The molecular characterization of cyanobacterial hydrogenases has continued. An up-to-date description of the present knowledge about both the uptake hydrogenase and the bi-directional enzyme has been presented (Tamagnini and Lindblad 2001). Maturation of [NiFe]-hydrogenases requires the action of several groups of accessory genes. Homologues of one group of these genes, the so called *hyp* genes, putatively encoding proteins participating in the formation of an active uptake hydrogenase in the filamentous, heterocyst-forming cyanobacterium *Nostoc* PCC 73102, have been cloned (Hansel et al 2001). The cluster, consisting of *hypF*, *hypC*, *hypD*, *hypE*, *hypA*, and *hypB*, is located 3.8 kb upstream from the uptake hydrogenase-encoding *hupSL*. Through a specific cooperation between Sweden and Portugal, a detailed overview has been compiled, and will be published in a leading international journal next year.

Initial bioreactor experiments, using wildtype and genetically modified strains have been presented. A mutant with the gene encoding the uptake hydrogenase inactivated evolves molecular hydrogen at a similar rate to a sulfur deprived green algae. Moreover, a method for examining "real competition experiments" between different strains, such as wildtype and a genetically modified mutant, has been developed.

Light-driven hydrogen evolution mediated by hydrogenase(s) was discovered in green algae over fifty years ago and subjected to extensive investigations over the following decades. However, there are still many fundamental and applied issues that must be addressed before this type of reaction can be considered for practical applications.

In Norway, a specific project on biohydrogen, sponsored by the Norwegian Research Council, was launched in 2001. The aim of the project is to develop know-how on new systems for sustainable energy production. The focus of the research is on biophotolytic hydrogen production by microalgae.

Activities during 2001 included establishing an operating test system to study the hydrogen production and screening of strains of green algae for suitable candidates for hydrogen production. Experimental work with various strains has been performed to gain experience on the adaptation process necessary for triggering hydrogen evolution. For this purpose both sulphur deprivation and addition of reducing agents have been applied to achieve sustained anaerobic conditions in illuminated cultures. In other experiments, evolution of hydrogen in the dark after degassing the cultures with nitrogen has been studied

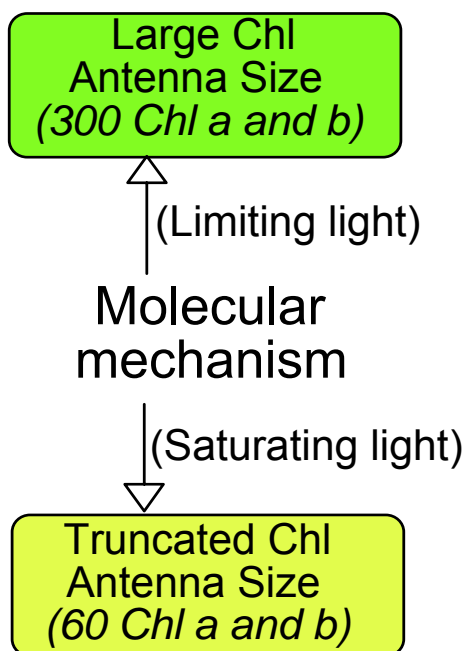
The initial results indicate large variation in the response on sulphur deprivation, and hydrogen production has so far only been observed in strains that have previously been reported to produce hydrogen by photolysis, e.g. *Chlamydomonas reinhardtii*. Lower yields of hydrogen were obtained from cultures of *C. reinhardtii* and *Chlorella fusca*, incubated in the dark.

b) Subtask B: Maximizing Photosynthetic Efficiencies

Photosynthesis can achieve relatively high solar conversion efficiencies, but only at low light intensity. At full sunlight, efficiencies drastically decline. The reason is the large amounts of so-called light-harvesting pigments, which capture more photons at full sunlight than the photosynthetic apparatus can actually handle. These excess photons are thus wasted, with their energy released as heat or fluorescence, even causing damage to the photosynthetic apparatus. Reducing antenna sizes is a method for increasing photosynthetic efficiencies, and this is a central R&D need in photobiological hydrogen production.

The goal of the present research, mainly carried out in the US, is to maximize the solar conversion efficiency and hydrogen production of photosynthetic organisms by minimizing, or “truncating” the chlorophyll antenna size of photosynthesis (see figure below).

Regulation of the Chl antenna size



The approach and objectives can be summarized as:

- i) A molecular genetic approach with the green alga *Chlamydomonas reinhardtii*
- ii) Identify and characterize genes that confer a “truncated Chl antenna size” in green algae

Work focuses on the identification of:

- i) Genes for pigment biosynthesis (Chl *b*, Lutein)
- ii) Genes for the regulation of the Chl antenna size

tla1 has been identified and characterized, the first-time isolation of a gene for the regulation of the Chl antenna size in photosynthesis. The picture below shows a greenhouse experiment in which growth and productivity (O₂ bubbling) in WT and *tla1* are compared. Note the higher cell density, lower amount of Chl and greater bubbling of the *tla1* relative to the WT.

Cultures in the Greenhouse



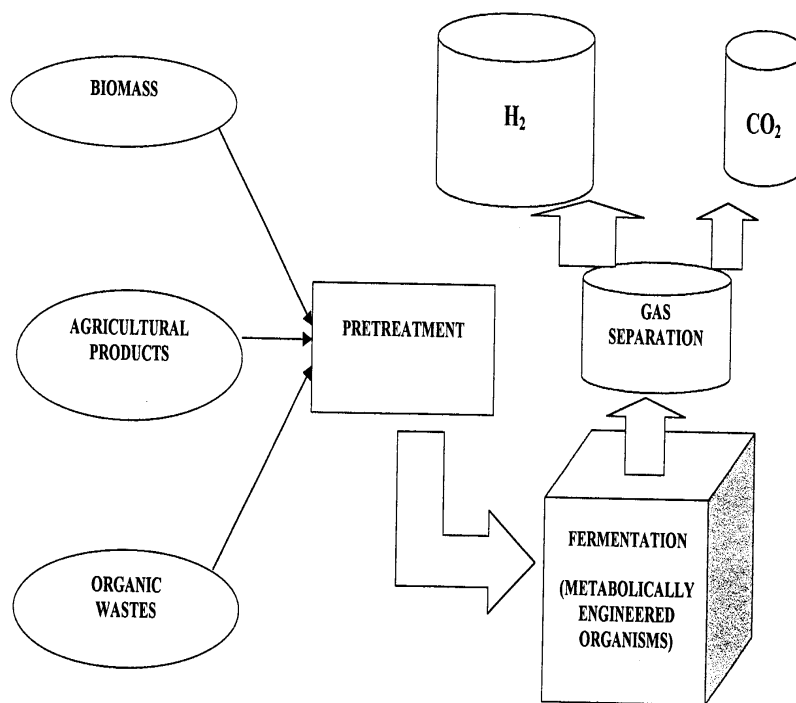
| <u>Parameter</u> | <u>WT</u> | <u><i>tla1</i></u> |
|--------------------------------------|-------------|--------------------|
| Cell/mL (x10⁶) | 6.36 | 10.0 |
| [Chl] (uM) | 25.6 | 15.4 |

c) Subtask C: Hydrogen Fermentations

After accumulation of carbohydrates, and activation of their inducible hydrogenase, a fermentation process is initiated in which storage carbohydrates are converted to hydrogen and a number of fermentation products, including acetate, glycerol, and other excreted substrates. Such fermentations have been reported in both green algae and cyanobacteria, but require

further study. At present, typical hydrogen yields from storage carbohydrates in the algae are less than 10%, based on a stoichiometry of 12 H₂/mole glucose.

In Canada, a team is being organized to develop an optimal system for the biological production of hydrogen through fermentation, using manipulation of microbial physiology, genetic engineering and advanced bioprocess engineering.



Fermentative processes, using either biomass obtained in a first-stage light-conversion process or perhaps more attractively, various waste streams, present an interesting, yet largely unexplored avenue for the biological production of hydrogen. Much is presently known about the molecular biology and biochemistry of the hydrogen producing enzymes, reductant generating systems and physiology of many hydrogen-producing organisms. The enormous potential of metabolic engineering for redirecting electron flux to hydrogen production in various microorganisms remains to be exploited. Very little is presently known about the currently attainable yields or the possibilities for improving these yields in the future. These questions will be addressed in currently proposed research activities.

The program will be multi-disciplinary involving researchers with expertise in recombinant DNA technology, biochemistry and microbiology, and chemical and bioprocess engineering. The research program, in which various avenues will be used to generate strains capable of high levels of hydrogen production, will involve several distinct phases over five years. Finally, near the end of the initial granting period, a conceptual system in which biohydrogen production is integrated with energy production (Fuel Cell) systems will be subjected to an energy balance analysis.

In the Netherlands, there are, at present, two projects on Biological hydrogen production. Both projects aim at the fermentative conversion of biomass (energy crops and organic waste streams) to hydrogen, employing extreme thermophilic and photoheterotrophic microorganisms. The research concerns the optimization of hydrogen fermentation processes and concomitant technological production methodologies.

Extreme thermophilic microorganisms ferment sugars to hydrogen and acetate (stage 1). With suspended cultures, 83% of the maximal theoretical conversion ($3.3 \text{ H}_2/\text{glucose}$) was obtained. The hydrogen production rates are similar to the fastest producers reported in the literature. Several extreme thermophiles are relatively tolerant to partial hydrogen pressures of up to $1\text{-}2 \cdot 10^4 \text{ Pa}$, making the thermofermentation process technologically feasible. For the process design, it also has to be considered that the microorganisms may have a relatively low tolerance for the by-product of fermentation, sodium acetate.

In the photoheterotrophic fermentation (stage 2) hydrogen must be produced from acetic acid. In this second year of the project, work focused solely on optimizing and modeling of photoheterotrophic growth and hydrogen production. The influence of three operational parameters on biomass growth and hydrogen production was investigated. The following parameters were taken into account: acetic acid concentration; molar ratio of acetate to glutamate; and light intensity (photon flux density). In addition, results from additional batch experiments were used to make carbon and nitrogen balances.

The yield of hydrogen on acetate ($Y_{\text{H}_2, \text{Ac}}$) was highest at a low ratio of acetate to glutamate ($C_{\text{Ac}}/C_{\text{Glu}}$). At a ratio of 5, $Y_{\text{H}_2, \text{Ac}}$ is between 37 and 43%. At a $C_{\text{Ac}}/C_{\text{Glu}}$ ratio of 10 or higher, glutamate appeared to be limiting biomass growth and hydrogen production. In additional experiments, it was found that all nitrogen (N), consumed as glutamate, is retrieved as biomass-N. These results support the hypothesis that hydrogen production from acetic acid is coupled to biomass growth.

The amount of carbon (C) consumed, on the other hand, could not be accounted for completely. Estimated balances of hydrogen (H) and oxygen (O) showed these elements also disappeared. The only explanation was the excretion of a dissolved product. Indeed, in additional experiments, it was found that there was a considerable increase in the chemical oxygen demand of the culture supernatant.

The influence of the light intensity was very small in the range of $270 - 620 \mu\text{mol PAR m}^{-2} \text{ s}^{-1}$. It appears that a light intensity of $270 \mu\text{mol PAR m}^{-2} \text{ s}^{-1}$ ($= 163 \text{ W m}^{-2}$, $400 - 950 \text{ nm}$) is sufficient to support maximal growth and hydrogen production.

Experiments focusing on electron transport processes and fermentative hydrogen production by enteric bacteria are presently being set up in Canada (Hallenbeck, unpublished).

d) Subtask D: Improve Photobioreactor Systems for Hydrogen Production

A major objective of applied R&D in photobiological hydrogen production has been the development of suitable photobioreactor systems. Development of such systems will serve as an intermediate step in the scale-up of hydrogen production from the laboratory scale to the commercial sector. A large number of different concepts and designs have been proposed and tested. However, there is a lack of engineering research for practical devices.

In a new UK-based project, "Feasibility study for the modification/optimization of energy efficient effluent treatment, pharmaceutical generation and clean energy production in photosynthetic organisms", the research team concentrates on both a *product* methodology (potential pharmaceuticals and **bio-hydrogen**) and *process* methodologies (pollution control), and how these interrelate, see Figure 1.

Publications

Hallenbeck, P.C. 2001. Integration of hydrogen evolving systems with cellular metabolism: the molecular biology and biochemistry of electron transport factors and associated reductases. In: Biohydrogen II, An approach to environmentally acceptable technology. Pages 171-184. Editors: Miyake, J., Matsunaga, T. and San Pietro, A. Pergamon/Elsevier, Oxford, UK. ISBN 0-08-043947-0

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Editors: Miyake, J., Matsunaga, T. and San Pietro, A. Pergamon/Elsevier, Oxford, UK. ISBN 0-08-043947-0

Seibert, M., T. Flynn, M.L. Ghirardi. 2001. Strategies for improving oxygen tolerance of algal hydrogen production. In: Biohydrogen II, An approach to environmentally acceptable technology. Pages 67-80. Editors: Miyake, J., Matsunaga, T. and San Pietro, A. Pergamon/Elsevier, Oxford, UK. ISBN 0-08-043947-0

Wakayama, T., J. Miyake. 2001. Hydrogen from Biomass. In: Biohydrogen II, An approach to environmentally acceptable technology. Pages 41-52. Editors: Miyake, J., Matsunaga, T. and San Pietro, A. Pergamon/Elsevier, Oxford, UK. ISBN 0-08-043947-0

Meetings/Conferences

Burja, A.M., MT. Bustard, P. Tamagnini and P.C. Wright, Specific Amplification of 16S rRNA gene segments from cyanobacteria and microalgae by PCR, COST 841 Workshop, Reading UK, March 2001

Burja, A.M., P. Tamagnini, and P.C. Wright, *Lyngbya majuscula* Bioprocess Intensification – Creating a Cell Factory, Society of Industrial Microbiology 2001 Annual Meeting, July 29 - August 2, 2001, Adam's Mark Hotel, St. Louis, USA

Hallenbeck, P.C. " Biohydrogen Production through Fermentation: Future Prospects and Studies with a Model System". 01-06-17. 11th Canadian Hydrogen Conference; Victoria, Canada

Lindblad, P. "Biohydrogen: International collaboration and Status & potential of using cyanobacteria". 01-08-22. 12th International Congress on Photosynthesis; Brisbane, Australia

Lindblad, P. "Cyanobacterial hydrogenases and biohydrogen: Present status and future potential" & "IEA H₂Agreement Task 15: *Photobiological Hydrogen Production* - An international collaboration". 01-06-19. 11th Canadian Hydrogen Conference; Victoria, Canada

Lindblad, P. "Cyanobacterial hydrogenases". 01-06-07. ESF Summer School *Cyanobacterial N₂ Fixation: Physiology and Molecular Biology*, Seville, Spain

Lindblad, P. "Photoproduction of H₂ by wildtype *Anabaena* PCC 7120 and a hydrogen uptake deficient mutant: From laboratory experiments to outdoor culture". 01-09-09. Biohydrogen, Joint workshop IEA Hydrogen Annex 15 & COST 8.41; Szeged, Hungary

Masuda T, Tanaka A and Melis A (2001). Annual Meeting of the American Society of Plant Biologists. Providence, Rhode Island, July 21-25, 2001

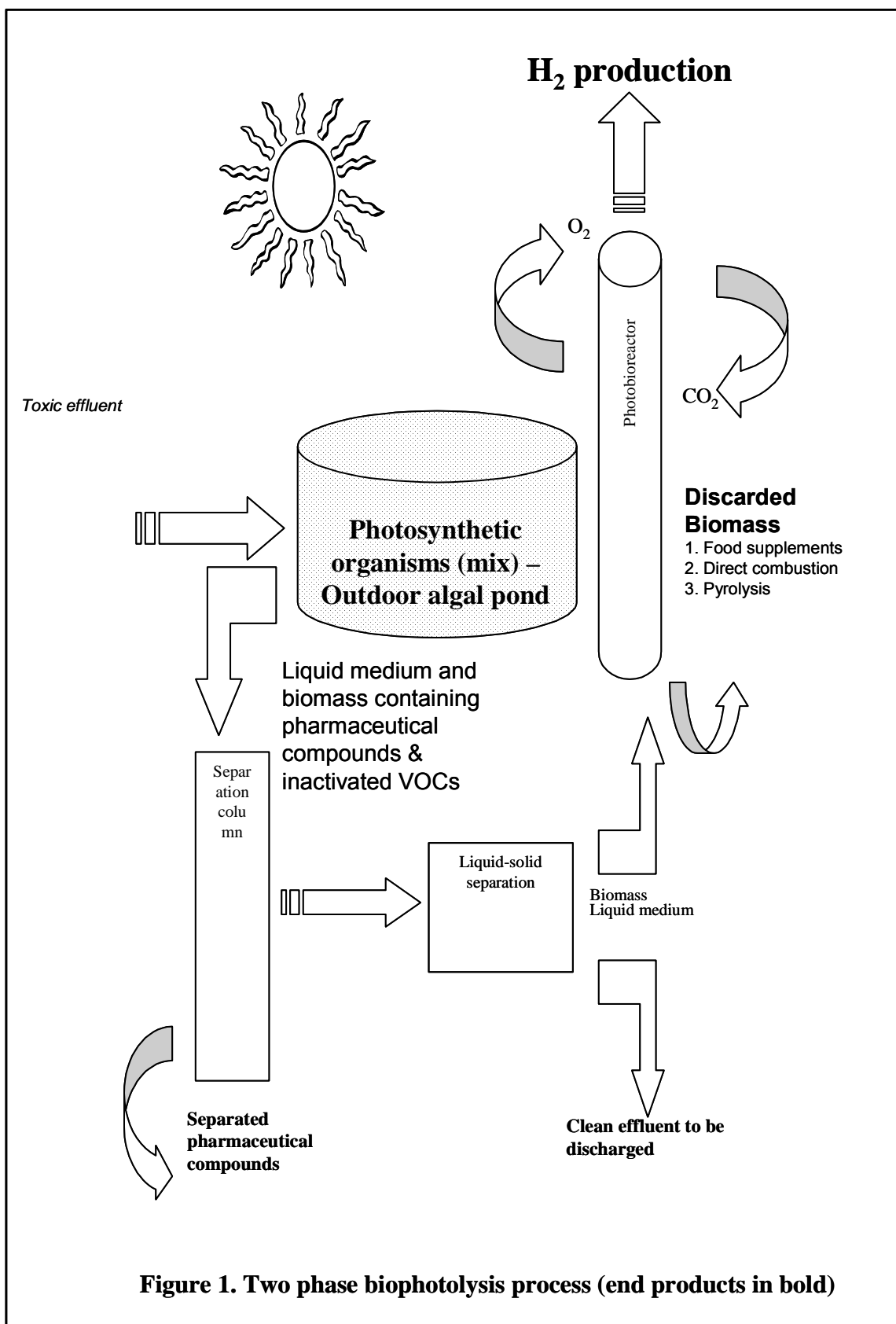
Melis A, Polle JEW, Kanakagiri S and Masuda T (2001) International Photosynthesis Congress, Australia, Aug. 15-18, 2001

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Tamagnini, P., A.M. Burja, E. Leitão and P.C. Wright, *hup* and *hox* genes in the filamentous non-heterocystous cyanobacterium, *Lyngbya majuscula* CCAP 1446/4 – Potential for large scale production, COST 841 Workshop, Reading UK, March 2001

Wright, P.C., M. T. Bustard, P. Tamagnini, A. M. Burja and B. T. Mohammed, “Integrated Bioremediation and Biofuels Generation: Characterisation of Enzymatic Reactions within Extremophiles”, *American Society of Microbiology*. May 20-24th, 2001 Orlando, Florida, USA.



TASK 17 – SOLID AND LIQUID STATE HYDROGEN STORAGE MATERIALS

Gary Sandrock

SunaTech, Inc.

Operating Agent for the

U.S. Department of Energy

Introduction

There are a number of technical and economic problems associated with the introduction of hydrogen as an alternate fuel. This Task is dedicated toward solving a key problem, hydrogen storage. Task 17 is derived from the successes of Task 12 (Metal Hydrides and Carbon for Hydrogen Storage) that was completed in 2000 and summarized in the 2000 Annual Report. The full Task 12 Final Report can be found at the IEA Hydrogen website:

<http://www.eren.doe.gov/hydrogen/iea>

Task 17 sets higher goals than Task 12, will explore a broader spectrum of hydrogen storage media and will involve a larger number of Experts and Projects. It began in June 2001 and is scheduled to continue until May 2004. Participating countries are Canada, Japan, Lithuania, Mexico, Norway, Spain, Sweden, Switzerland, United Kingdom and United States.

Task Targets, Materials and Project Types

The Task is oriented towards the development of new reversible hydrogen storage media with increased gravimetric and volumetric capacity, along with the development of fundamental understandings of those materials so as to continue efficient R&D progress. The main application of interest is vehicular hydrogen-storage, although that should not be considered our sole interest. The two targets are as follows:

1. Develop a reversible hydrogen storage medium with 5 wt.% H₂ recoverable at < 80°C and 1 atm absolute pressure, with charging and discharging rates suitable for practical use.
2. Develop the fundamental and engineering understanding of hydrogen storage by advanced hydrogen storage media that have the capability of meeting Target 1.

The types of hydrogen-storage media of interest to the Task include the following:

- Non-traditional hydrides (e.g., catalyzed complexes)
- Carbon (all forms: nanotubes, nanofibers, fullerenes, activated charcoals, other forms of nanoporous carbon, etc.)
- Other nanoporous materials
- Rechargeable organic liquids and solids
- Rechargeable inorganic liquids and solids

The projects encompass the following categories:

- Experimental

- Engineering
- Theoretical
- Modeling (scientific or engineering)

National Participations

Following are the current participating countries, experts and organizations:

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List of Projects

Task 17 consists of series of R&D projects led by project leaders from participating countries. Most involve international collaborations among participating individuals and institutions. The following is a list of the active Task 17 projects:

Carbon Projects

•Proj. C-1. Hydrogen storage in single-wall carbon nanotubes (R. Chahine [Canada] and M. Heben [USA])

This joint project involves collaboration between two pioneering North American hydrogen-on-carbon laboratories. It aims at comparing the hydrogen absorption/desorption properties of well-characterized single-wall carbon nanotubes (SWNT) by three precision techniques: volumetric, gravimetric and temperature-programmed-desorption.

•Proj. C-2. Hydrogen storage in carbon nanotubes (T. Mays [UK])

This project will look toward the synthesis and processing of carbon nanotubes relative to the optimization hydrogen-storage properties. It will include optical and transmission electron microscopy characterization of nanotubes and theoretical calculations and simulations to aid interpretation of the hydrogen adsorption data obtained.

•Proj. C-3. High-pressure X-ray diffraction measurements of hydrogen in nano-structured carbon (P. Hall [UK])

Graphite nanofibres will be synthesized and studied by high hydrogen-pressure neutron diffraction, inelastic neutron scattering and positron annihilation studies to understand how hydrogen is absorbed. It is hoped that H_2/D_2 pressures up to 200 bar can be achieved.

•Proj. C-4. *No longer active*

•Proj. C-5. Hydrogen storage in carbon-based materials (R. Jones [UK])

Dstl Farnborough and its contractors are studying the catalytic synthesis of gram quantities of carbon nanofibres and multi-wall nanotubes for hydrogen storage. Modeling suggests the theoretical possibility of 14 wt.% H_2 at ambient temperature and 40 bar pressure.

•Proj. C-6. Modified carbon nanotubes for hydrogen storage (R. Zidan [USA])

Carbon nanotubes doped with nanoparticles will be synthesized and evaluated for hydrogen storage. Nanoparticles and clusters are hoped to facilitate the polarization and condensation of hydrogen within nanotube bores and nanotube clusters.

•Proj. C-7. *No longer active*

•Proj. C-8. Enhancing the hydrogen storage capacity of carbon nanofibres (G. Walker [UK])

The aim of this project is to modify the surface of graphite nanofibres to maximize hydrogen absorption capability. This includes the elimination of amorphous carbon, graphitic caps and other natural surface species, in order to control the surface chemistry.

Combined Hydride + Carbon Projects

•Proj. HC-1. H-storage in nano-structured carbon-related materials and hydrides (H. Fujii and S. Orimo [Japan])

This project is exploring two areas: (1) the production of nanostructured graphite and boron nitride by ball-milling techniques, and (2) the production of nanocomposites by sputtering techniques. The presence of nanoscale grain boundaries and composite boundaries may result in improved hydrogen storage behavior.

•**Proj. HC-2. Hydrogen storage in metal hydrides, nanotubes and carbon** (S. Gamboa and J. Sebastian [Mexico])

This project will concentrate on the electrochemical storage of hydrogen for application in batteries. Both metal hydrides and various forms of carbon will be investigated. The carbons will include nanotubes and fullerenes.

•**Proj. HC-3. Structural characterization of hydrogen storage materials** (B. Hauback [Norway])

Hydrogen storage materials will be characterized by neutron scattering techniques using the IFE research reactor and associated spectrometers. This work will be performed on Task 17 materials submitted by other laboratories, as well as some IFE-developed materials.

•**Proj. HC-4. No longer active**

•**Proj. HC-5. H-storage in nanostructured carbon and metals** (A. Züttel [Switzerland])

The hydrogen storage capability of both metal hydrides and carbon will be studied using PC isotherms, thermal desorption spectroscopy and thermogravimetry, as well as in situ neutron and X-ray diffraction and photoelectron spectroscopy. There will be some concentration on the catalyzed alanates and transition metal complexes.

•**Proj. HC-6. No longer active**

•**Proj. HC-7. Development and characterization of advanced materials for hydrogen storage** (M.A. Imam [USA])

A variety of nanostructural metallic and carbon materials will be synthesized and evaluated for hydrogen storage capability and various characterization techniques, e.g., X-ray, electron and neutron diffraction, SEM, HRTEM, STEMP, EELS and TGA. The project will be augmented with fundamental simulation and modeling techniques.

•**Proj. HC-8. Engineering properties of new storage materials** (G. Thomas [USA])

This project is divided into two areas: (1) determination of material properties such as kinetics, thermodynamics, thermal conductivity, heat capacity, expansion, etc. and (2) parametric modeling of bed designs to predict performance. The work will begin on alanate beds and later move to carbon beds when multigram quantities of reproducible carbons become available.

•**Proj. HC-9. Hydrogen in hydrides, carbon and zeolites** (D.K. Ross [UK])

This project covers a number of research and ab initio calculation areas for carbon and hydrides, as well as some novel H₂ absorbers such as zeolites. Techniques to be used include gravimetric analysis and neutron scattering.

•**Proj. HC-10. Fabrication of hydrogen storage alloys and composites employing vapor deposition technologies** (D. Milcius [Lithuania])

Vapor deposition technologies (e.g., sputtering and arc discharge deposition) will be used to produce metastable materials and nanocomposites with grain sizes less than 100 nm. It is hoped that hydrogen-capacity and thermodynamics can be improved over conventional materials. Both hydrides (e.g., alanates) and carbons will be studied.

Hydride Projects

- Proj. H-1. IEA/DOE/SNL on-line hydride databases** (G. Sandrock [USA] and S. Mitrokhin [at large])

IEA Task 17 maintains a public on-line Hydride Information Center with an extensive series of databases (<http://hydpark.ca.sandia.gov>). The existing databases will be updated and new ones created. The effort will also try to capture more of the Russian language hydride literature.

- Proj. H-2. Real time synchrotron and neutron studies of hydrides** (J. Huot [Canada])

This project will use in situ synchrotron XRD and neutron studies to determine sorption and desorption mechanisms of hydrides. Composite hydrides and alanates will be studied.

- Proj. H-3. Alkaline borohydride solutions as H-generation system** (S. Suda [Japan])

This project is studying the use of NaBH_4 in liquid solution as a source of hydrogen that can be generated by catalyzed hydrolysis. An important part of the research will be to learn how to regenerate the spent NaBO_2 back to the starting borohydride at reasonable cost and energy efficiency.

- Proj. H-4. Zintl phase hydrogen absorbing compounds** (E. Akiba [Japan])

Zintl phases (e.g., SrAl_2) have recently been shown to form hydrides (e.g., SrAl_2H_2) that are intermediate between the metallic (interstitial) and ionic-covalent complex hydrides. This project is studying the possibility that this new class of hydrides may offer properties of practical value for hydrogen-storage.

- Proj. H-5. Research of new X-TM-Y alloys (X=Ca, Mg, Li; TM=transition metals; Y=metals)** (N. Kuriyama [Japan])

This project will survey ternary alloys based on low-cost Ca, Mg and Li in hopes of finding new systems with practical storage potential. Initial work will be on Ca systems and will focus on PCT properties, crystal structures and disproportionation resistance.

- Proj. H-6. Nonconventional hydrides with low H-H separations** (V. Yartys [Norway])

IFE has recently discovered new hydrides that have record low H-H distances (e.g., $\text{R}_3\text{Ni}_3\text{In}_3\text{H}_4$). This may offer a path to compact new hydrogen-storage materials. Experimental work will include in situ neutron diffraction and synchrotron XRD studies of the new structures.

- Proj. H-7. Destabilization of hydrides based on hydride complexes** (D. Noréus [Sweden])

Work will be continued on Mg_2NiH_4 with the object of weakening the Ni-H bond strength of this complex hydride. Other complexes involving Ni-H arrays will also be studied. In addition to measuring PCT properties, optical properties will be also studied as a means of understanding the fundamental electronic and phase transitions involved.

- Proj. H-8. Destabilization of metal hydride complexes and theoretical modeling** (K. Yvon [Switzerland])

Attempts will be made to decrease the desorption temperatures of complex hydrides such as Mg_2FeH_6 and Mg_3MnH_7 . This will include elemental substitutions and catalysis (the latter to be done in concert with Project H-10). Attempts will also be made to develop a theoretical model for the stability of the complex metal hydrides.

•Proj. H-9. Thermal hydrogen compression with purification (D. DaCosta [USA])

A pilot scale thermal hydride compressor will be designed, built and tested. In particular, the compressor will include internal purification means so that low purity H_2 can be compressed and simultaneously purified. Impurities to be tested include H_2O , CO , CO_2 , N_2 and CH_4 .

•Proj. H-10. Catalytically modified hydriding properties of novel complex hydrides (K. Gross [USA])

In concert with Project H-8, the TM complex hydrides Mg_2FeH_6 and Mg_3MnH_7 will be catalyzed with Ti, which is very effective as an absorption/desorption catalyst for the alanates $NaAlH_4$ and Na_3AlH_6 . Catalyst enhanced reversibility of TM and other complex hydrides could provide the next leap forward in practical hydride materials.

•Proj. H-11. Solid-state nuclear magnetic resonance spectroscopic studies of catalytically enhanced sodium aluminum hydride (C. Jensen [USA])

The mechanism by which species like Ti and Zr positively influence the kinetics of the sodium aluminum complex hydrides is unknown. This project will use NMR spectroscopy to seek out the identity and role active “catalytic” species. Knowing that should help in further improvement or optimization of doped Na-Al hydrides.

•Proj. H-12. Electronic design and mechanochemical synthesis of new hydrogen absorbing materials (Z.X. Guo [UK])

The scientific objective of this project is to investigate the effects of alloying and processing on the hydrogen-storage properties Mg-alloys and Na-alanates, using first principles, electronic structural simulations and molecular dynamics. The technological objective is to use mechanochemical powder metallurgy techniques to synthesize those hydride compositions predicted to have useful properties.

•Proj. H-13. Hydrogen storage for fuel cell vehicle based on $NaAlH_4$ (D. Anton [USA])

The ultimate objective of this project is to build and test a sodium-alanate bed capable of supplying 5 kg H_2 for a fuel cell vehicle. To accomplish this, improvements in alanate properties and understandings of safety and engineering properties must be developed. The gravimetric target for the system is 6 wt.% H_2 , so that the hydrogen-storage medium itself should carry at least 7.5 wt.% H_2 .

Experts' Workshops

Two successful Experts' Workshops have been held thus far: 10-11 July 2001 at New London, CT, USA and 21-22 February 2002 at Seattle, WA, USA. A third Workshop is planned for 9-11 September 2002 at Geneva, Switzerland.